ELEMENTARY CHEMISTRY

BOOK II

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ELEMENTARY CHEMISTRY

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Book II

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PREFACE

At first sight it seems curious that the general reader seldom includes a popular Chemistry among the books he reads, though he may have enjoyed Ball's "Story of the Heavens", Wells' "Science and Life", "Bragg's "World of Sound", and other works dealing in a readable way with one or more other branches of science. Yet the reason for the comparative unpopularity of chemistry with the general reader is really not far to seek. It is simply that a writer of "popular" chemistry finds it hard to proceed far without using a language which is foreign to the reader,—the language of equations; and nobody can care much for a book if some of its most important passages are expressed in a language which he does not understand.

But what are we to say of the many people who have "learnt"chemistry and its equational language at school, and who none the less in later life avoid books of the "Everyday Chemistry"[1] type? The answer is that while their school chemistry placed great emphasis on equations and on formal chemistry generally, it failed to make them realize that the subject is connected at a thousand points with the daily life around them. As a result, they left school with little inclination to extend their knowledge of this branch of science.

It seems clear then, that while a school chemistry course must be thorough in its treatment of the basic principles and what we have called the "language" of the subject, it must also keep constantly in view the countless connections

[1] No particular book is indicated.

of which we have just spoken,—it must have regard to "applied" as well as to "pure" chemistry. There is, of course, nothing new about this conclusion, but very few books appear to have been written in which a good balance has been maintained between the two. The present course represents a serious effort to maintain such a balance. As it is intended for Canadian boys and girls, it seemed obvious that illustrations would be more forcible and interesting if drawn from Canadian industries, natural resources, etc., and this has been done to a very large extent.

It is assumed that a first year chemistry course has already been taken, but I thought it advisable to begin by recapitulating the more important underlying principles. This has been done in the first chapter.

Opinion is somewhat divided as to the point at which the subject of Atomic Structure should be introduced, and many excellent teachers would take it in immediate connection with the Periodic Law. I have given it a much later position, for reasons into which I will not enter, because to do so would unduly prolong this Preface. However, no difficulty need arise in practice, for a teacher who believes in earlier treatment can quite easily take Chapters XXVII and XXVIII ("Radium" and "The Structure of the Atom") immediately after VI ("The Periodic Law").

Most teachers are agreed that the quantitative side of the subject should be kept constantly in view, and so the questions with which each chapter closes usually include a few straightforward calculations. It is taken for granted that the course will be accompanied by practical work. No teacher, however, likes to spend much of the limited time available in dictating practical notes, cautions, etc., and for this reason a short "Laboratory Manual" has been drawn up containing practical details of the more essential experiments.

I am much indebted to various government officials, secretaries of companies, etc., for help in obtaining illustrations, and when reproducing these I have made the usual

courtesy acknowledgment. I must also thank the following who have supplied me with useful information:—Mr. R. H. Coats (Dominion Statistician), Mr. L. H. Cole (Mineral Resources Division, Department of Mines, Canada), Mr. J. D. Galloway (Provincial Mineralogist, Bureau of Mines, Victoria), Mr. E. M. Lynch, Department of Natural Resources (Canadian National Railways), Mr. Colin Groff (Publicity Commissioner of the Province of Alberta), Mr. W. Calder (Department of Lands and Mines, Edmonton), Mr. H. S. Watts (of the Canadian Western Natural Gas, Light, Heat and Power Co. Ltd.) and Mr. G. C. Ommaney (Director of the Department of Development, Canadian Pacific Railway Co.). The editor of *The Journal of the Society of Chemical Industry* assisted me by putting me in touch with good sources of information, and so did the editor of *The Industrial Chemist and Chemical Manufacturer.* Thanks are also due to Messrs. Geo. Bell & Sons Ltd., the publishers of two of my earlier books, who very kindly allowed me to use a considerable amount of the material contained in them. Further, I would like to recognize the assistance of three of my senior science students (P. R. J. Barnes, E. G. Hebditch and A. F. Pym) who corrected the proofs in points of detail, and of my nephew (Mr. Arthur Littler of Windsor, Ont.) who kindly undertook a further revision of them. Finally I must thank Mr. G. F. Hollinshead of Calgary and Mr. H. E. Tanner of Edmonton, both of them practical teachers, who greatly helped me by suggestions and by their very full replies to a long list of queries which I addressed to them.

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INTRODUCTION

THE USEFULNESS OF CHEMISTRY

Most of the boys and girls who are beginning to read this book will already have spent some time in studying the simpler parts of chemistry, and it is well that at this point we should leave detailed work for a little while and try to think of the subject in a more general way.

Paul of Tarsus seems to have had a quite proper pride in the fact that he was " a citizen of no mean city ", and it is the purpose of this introduction to help you to realize that you are a student of no mean subject; that chemistry is indeed a subject to be proud of, partly because it has been, and is being, of the utmost service to mankind.

We say "partly", because it cannot too often be insisted upon that the true scientist studies chemistry *for its own sake* and not simply for the material benefits that the study brings in its train. Actually most of us love "knowledge for its own sake" far more than we think we do. You have noticed a little boy standing by while his father mends the radio or changes a tire. The child asks lots of questions. No doubt in years to come the answers to those questions will help him when he is doing jobs on his own account, but *that is not why he asks them.* He asks them simply to satisfy his curiosity, — *he wants to know.* That is exactly the attitude of the true scientist, and the experiments he makes have been well described as questions addressed to nature.

At the same time, the subject of the actual usefulness of chemistry in the daily life of man is a very interesting one, and we may now briefly consider a few examples. We shall begin with the important question of food supply.

In 1898 Sir William Crookes, one of the world's greatest scientists, aroused widespread alarm by an address which he made to the British Association. In this address he drew attention to the fact that the world's demands for wheat were continually increasing, and that the soil was able to produce this wheat only if it were regularly supplied with "fixed nitrogen", *i.e.* not the nitrogen of the air, which is in the free condition, but nitrogen in combination with other elements. The only really large supply of fixed nitrogen consisted of "Chile saltpetre" — sodium nitrate, $NaNO_3$. Sir William estimated that the supplies of this would begin to run short by the year 1930 or thereabouts, and after that time the earth would be unable to feed its population; we should be faced with world famine. He suggested that chemists should try to find some way of making the nitrogen of the air combine with other elements, so turning it into the necessary fertilizer.

His advice was taken, and several very successful processes have been worked out. In the one chiefly in use, atmospheric nitrogen is made to combine with hydrogen, forming the gas ammonia, NH_3. From this it is a very easy matter to prepare ammonium sulphate, a substance which, by the bacteria present in the soil, is readily turned into the necessary nitrates.

As it turns out, the situation would not in any case have become serious as early as 1930, because the world's extra needs have been met by bringing additional land under cultivation —land which at one time was thought to be too dry, or too cold, for growing wheat.[1] Still, there is of course an end to this supply of extra land, and we may be very glad that we have at hand an unlimited source of

[1] Crooks calculated that in 1928 there would be 256 million acres producing wheat. Actually the number was 306 millions.

nitrates, so that we can restore to the soil the constituents which the wheat is constantly taking from it.[1] If chemists had not discovered how to make nitrates artificially, the day would have come when we should have been obliged to buy our nitrates in South America at any price the Chilean Government liked to fix, and the price of bread would have gone up and up. Later on the supplies of nitrate would have become exhausted, and the world famine which Crookes foresaw would really set in.

Perhaps the schoolboy of the far-distant future will learn as one of his important dates *not*

1066 —William the Conqueror invaded England, but
1898 — Sir William Crookes called attention to the need for synthetic nitrates.

Leaving the question of artificial fertilizers, let us turn for a moment to the question of soap manufacture. This substance is made by boiling fat (*e.g.* mutton fat) with caustic soda. The soap manufacturer can make use of many kinds of fat, but until lately he had to reject thousands of tons of cheap fish oil — it would not make good soap. It was known that the chemical difference between the liquid oil and the solid fat was simply that the oil contained less hydrogen, but nobody knew how to make the oil combine with an extra amount of this element. At last a chemist named Sabatier found that if he heated the oil with hydrogen *in the presence of finely divided nickel* the necessary combination took place. Not only soap, but margarine of excellent quality is now being made from fats prepared from cheap oils by this new process. It seems rather unfair that, although shareholders in industries connected with fats and oils have made fortunes out of Sabatier's discovery, the chemist himself received none of the proceeds, and except in scientific circles few people have even

[1] There is no doubt that by the application of nitrates the average yield per acre could be largely increased if necessary. Canada possesses excellent soil for wheat, but produces only 16·6 bushels per acre. Denmark, with a generous use of fertilizer, produces 36·3.

heard his name. "Solid fats from liquid oils, edible fats from whale and fish oils, a fortune for the whaling industry made literally overnight, and yet I vouch that no captain of a whaler or shareholder in a whaling company has ever heard of the name of Sabatier.[1]"

Another great industry which depends at every turn on chemical discovery is that of artificial silk, which is made from *wood*. On the railway sidings of a big silk-factory one can see an incoming line of cars loaded with wood-pulp, which has been made perhaps from the trees of Quebec or Ontario, and from the shipping sheds a few hundred yards distant other cars carrying away artificial silk of every colour.

We must notice that, though in this case the artificial product in many ways *resembles* the real article, it is not the *same thing*. It has a quite different chemical composition. Often enough, however, the product of the chemist is exactly the same as that of nature. Take indigo, for instance, the well-known blue dye. Until 1897 it was prepared exclusively from the indigo plant which grows in India, but a German chemist named Baeyer set himself the task of making the substance in the laboratory. Its formula was known to be $C_{16}H_{10}O_2N_2$, giving carbon 73·3 per cent., hydrogen 3·8, oxygen 12·2, and nitrogen 10·7. But Baeyer knew that it was as hopeless to expect to produce indigo by mixing carbon, hydrogen, etc., in the correct proportions, as it would be to expect to make a house by mixing up bricks, wood, plaster, etc., in the correct proportions. A house has a definite *structure*, and so has the molecule of indigo. One great difficulty is that while the builder can see a house, the chemist cannot see a molecule.

However, after fifteen years of patient work, Baeyer succeeded in his task,[2] and since then indigo has been made

[1] Lecture delivered in Glasgow by Dr. E. F. Armstrong, February 14, 1930.

[2] At least he laid the foundations. The practical process finally adopted is due to Heumann.

on a large scale with the use of naphthalene (the "moth-balls" obtained from coal-tar) as the principal raw material. Synthetic indigo is the *same thing* as the purified natural product, and can be made at less than half the price. Thus, indigo-dyed clothing is cheaper than it otherwise would be, and a great area of land formerly required for the cultivation of indigo can now be used for the production of other crops.[1]

We must glance very briefly at the subject of metals. For the most part these do not occur free in nature, but have to be extracted from their ores, and the chemist is constantly devising new methods and improving old ones. Of late years he has been turning his attention more particularly to the preparation of alloys, and one of his most popular successes has been the "stainless steel" now so widely used for articles of cutlery. Then there is "duralumin", an alloy consisting of 95 per cent. aluminium, 4·5 per cent. copper, and small quantities of magnesium, manganese, and iron. We all remember the famous duralumin mast which helped the Americans to beat *Shamrock V* in September 1930, and perhaps wish that, for once, the chemist had been just a little less busy. We must not forget nickel. Of late years this metal has been largely used for the production of various "nickel steels", most of which show the property of extreme hardness without brittleness. Nickel steel was largely used in construction of *"The Golden Arrow"*, the car in which the late Sir Henry Segrave set up his remarkable record of 231·36 m.p.h. Probably no ordinary steel would have stood the strains to which a car travelling at such a speed would be subjected.

Very often it happens that a great advance in some other branch of science (or art) is only possible because of some earlier discovery made in chemistry. Examples of this are particularly numerous in medicine and surgery, and a

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[1] The area of land under indigo fell from 977,349 acres in 1900 to 67,300 acres in 1930, a reduction of 93 per cent.

familiar one is the use of chloroform ($CHCl_3$), discovered by the chemist Liebig in 1831, but first used as an anaesthetic by Sir James Simpson in 1847.

Before 1847 serious operations were comparatively rare because of the unbearable pain. Now that they could be carried out painlessly they became much more common — and then another very serious trouble arose. In hundreds of cases the wound of the operation became what we should now call "septic" — poisoned in some way that the doctors could not then understand — and the patient died of what was often called "hospital gangrene".

A great surgeon named Joseph Lister believed that the gangrene was caused by a certain germ getting into the wound and multiplying at a great rate. If he could kill the germ, he ought to be able to save the patient's life. Once again it was a product of chemistry which saved the situation, for Lister discovered that germs could not live in carbolic acid or phenol, C_6H_5OH. By the proper use of a solution of phenol the wound was kept free from germs and soon healed up. There is no need to make exaggerated claims. Lister's discovery was, first and foremost, a triumph of surgery, but it was chemistry which provided him with an essential weapon. If we say that his discovery has saved thousands of lives, we are certainly well within the mark, and probably we should not be going beyond it if we said millions.

Even beyond the borders of our ordinary civilization chemistry can still be of the utmost use, as the following illustration will show — an illustration connected with the age-long disease of leprosy.

It has been known for a long time that sufferers from this terrible disease derive benefit from a substance known as chaulmoogra oil, but the oil is so utterly sickening that patients can only take small doses, much too small to be of real use. The doctors tried injecting the oil into the patients' veins, but large doses still produced sickness. A few years ago it occurred to them that chaulmoogra oil was

By courtesy of Imperial Chemical Industries.

very likely a mixture of many substances, and that perhaps the benefit was obtained from just one or two constituents of the mixture. An able chemist was called in tc help, and he succeeded in splitting up the oil into a large number of different constituents. The doctors tried these separately, and soon found that the curative effect was due to only two of them — two acids. The chemist now got to work on these acids, and soon managed to modify them in such a way that their curative powers were not reduced, and yet patients could stand much larger injections. Some wonderful results are being recorded, especially in the earlier stages of the disease. A leper settlement in Hawaii reports 53 per cent. of cures among 399 patients treated, and it is calculated that, in those islands, in another twenty-five years, leprosy will be practically a disease of the past.

We have considered just a few of the ways in which the study of chemistry has been useful to mankind in general, but a moment's thought will show us that the subject is of quite outstanding importance to Canada. For Canada is a country of vast natural resources, and the problem of their wise utilization is in great part a chemical problem. One thinks of the immense and varied metalliferous ores of Ontario and other provinces, of the vast areas of forest, of the great reserves of oil and natural gas in Alberta, of millions of units of water-power already harnessed and millions more awaiting development. One thinks, too, of the abundant supplies of salt in Nova Scotia, calcium carbonate at Camperville, of deposits of sodium sulphate in Saskatchewan estimated at 120 million tons. Elsewhere we have quantities of asbestos and mica; of gypsum, graphite, mica . . . but the list is well-nigh endless.

And these natural resources are the raw material of the chemist, who is already turning wood into silk, salt into chlorine and caustic soda, sulphur (from metalliferous ores) into ammonium sulphate that will re-fertilize the wheat fields of the prairie, and so on. Governments, both Dominion and Provincial, are showing themselves alive to the re-

sponsibility for dealing wisely with their native wealth. Their efforts will only be fully seconded, however, when some knowledge of chemistry and its applications is widely diffused throughout the mass of the people.

But though in a country like Canada the wide-spread study of chemistry may well result in increased material gain, it is not for such a reason that it has been made a subject of school study. Its place there is due to the fact that it is one of the great sciences, and that the study of science, — for its own sake, as we said at the beginning, —is an important element in human culture.

CHAPTER I

IMPORTANT POINTS REVIEWED

It was common enough during the Great War to read passages such as "Before making a fresh advance we decided to consolidate the positions already won." That is evidently a very sensible course to adopt, and there is a place for it in the study of chemistry as well as in war. Let us then before attempting any further advance, glance at some of the outstanding points in our earlier work and try to "consolidate the positions".

We shall begin with the **Law of Constant Proportions.**—*"A given chemical compound always has the same composition, no matter by what process it is made."* Copper oxide will furnish us with a very good example, for we can make it

(1) by dissolving copper in nitric acid to make the nitrate, then evaporating to dryness, and decomposing the nitrate by the action of heat, leaving the oxide—

$$(a)\quad Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2,$$
$$(b)\quad 2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2;$$

(2) by dissolving copper sulphate in water, and adding a solution of sodium hydroxide to precipitate copper hydroxide. The liquid is then boiled to decompose the hydroxide into oxide[1], and the latter is filtered, washed, dried, and finally heated to redness—

$$CuSO_4 + 2NaOH \rightarrow Cu(OH)_2 + Na_2SO_4,$$
$$Cu(OH)_2 \rightarrow CuO + H_2O;$$

[1] The decomposition is really not quite complete at this stage, but is completed on heating just to redness.

(3) by proceeding in the way just described, but using a solution of sodium carbonate instead of sodium hydroxide. This causes copper carbonate to be precipitated, which is decomposed by heat into the oxide.

We now take our three specimens of copper oxide, — prepared by three distinct methods, — and reduce them in a stream of hydrogen or coal gas in the manner indicated

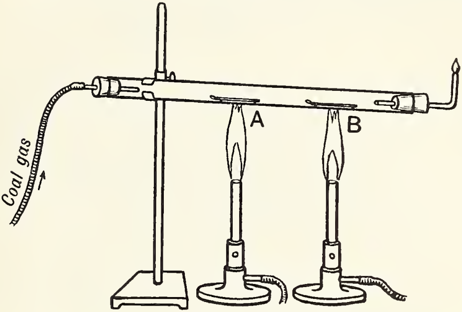

Fig. 1.—Illustrating the Law of Constant Composition.

in the diagram. (It may be possible to put all three boats into the combustion tube at the same time, but that, of course, is not essential.) We might very well put the same weight of each specimen in the respective porcelain boats. After reduction each boat is found to contain the same weight of copper. Thus the three specimens all contain the same percentage of copper, and therefore (by subtraction) the same percentage of oxygen,—so we have proved our point.

At this stage you should work out questions 1 and 2 at the end of this chapter. It will help to give you a firmer grip of the law we have been discussing.

We now come to the **Law of Multiple Proportions**:—*If two elements combine to form more than one compound, and the weight of one of the elements is the same in each,*

then the weights of the other element will be in a simple ratio to each other.

Most people find this law a little puzzling, so let us study the following additional example.

Copper forms two oxides, a black one in which the percentage of oxygen is $20 \cdot 1$, *and a brown one in which it is* $11 \cdot 2$. *Show that these numbers illustrate the Law of Multiple Proportions.*

We may arrange our calculation like this:—

	Oxygen	*Copper*		*Oxygen*	*Copper*
Black oxide . . .	20·1	79·9		1	3·97
			or		
Brown oxide . . .	11·2	88·8		1	7·93

(The first two columns simply express the given information in tabular form. In the third column we make " the weight of one of the elements the same in each " by dividing by 20·1 in the first case and 11·2 in the second. Evidently the weights of copper must be reduced in the same proportion, so we divide 79·9 by 20·1 getting 3·97, and 88·8 by 11·2 getting 7·93.)

Now 7·93 and 3·97 are in the simple ratio of 2 : 1, and so the law is illustrated.

(N.B.—The " simple ratio " is of course not always 2 : 1. It might be 3 : 1, 3 : 2, etc.)

It would be a good plan now to work out one or two of the questions on page 21, 5 and 6, for instance.

Physical Laws Relating to Gases.—These are chiefly **Boyle's Law** *which states that*: *If the temperature of a given mass of gas remains constant, its volume will vary inversely as the pressure, and* **Charles' Law** : *If the pressure of a given mass of gas remains constant, its volume will be proportional to its absolute temperature.*

The following example involves the application of both these laws :—

If 380 *c.c is the volume of a quantity of hydrogen when the temperature is* 12°*C. and the barometer reads* $74 \cdot 0$ *cm., what would be the volume at N.T.P.?*

We put down the given volume (380 c.c.) and first allow for change of temperature, as though there were no change of pressure, thus getting $380 \times \frac{273}{285}$.

We next allow for change of pressure as though there were no change of temperature. At pressure 76 cm. the volume would evidently be *less* than at pressure 74, so we multiply by $\frac{74}{76}$.

$$\text{Thus, required volume} = 380 \times \frac{273}{285} \times \frac{74}{76} = \mathbf{354 \cdot 4\ c.c.}$$

N.B.—In all temperature and pressure calculations, it is a good plan before "multiplying out", to make sure that the standard numbers 273 and 76 are on opposite sides, *i.e.* if 273 is in the numerator, 76 must be in the denominator and *vice versa*. If this is not the case there is something wrong.

Vapour Pressure.—Although the following section is not strictly a "review" because some new ideas are introduced, it will be convenient at this point to consider another physical law relating to gases (and vapours).

AB is a barometer made by filling a tube about a yard long with mercury, and inverting it in a dish of that liquid. The mercury falls a few inches to the point *C*, the height of the column *BC* (somewhere about 30 inches) being a measure of the atmospheric pressure at the time of the experiment.

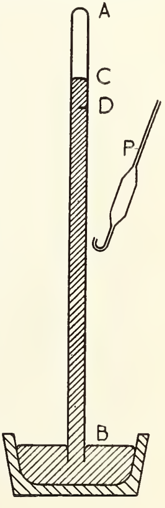

Fig. 2.

By means of a very small curved pipette *P*, a minute quantity of water is introduced into the space *AC*. It quickly vaporizes, and the mercury is pushed down a few millimetres, say to *D* (*CD*, however, is much exaggerated in the figure for the sake of clearness). Suppose *CD* were 3 millimetres, then the pressure of the water vapour is clearly equal to that of 3 mm. of mercury.

If more water is introduced the mercury is pushed down further still, but a point is soon reached at which the space is *saturated* with water vapour. When this is the case, the addition of

more water produces no further effect, the added liquid simply lying unvaporized on the top of the mercury. If the temperature at which the space was saturated were 15°C., the mercury would actually be pushed down 12·7 mm., and we, therefore, say that "the maximum pressure of aqueous vapour at 15°C. is 12·7 mm." ("of mercury" being understood). We speak of *maximum* pressure because the pressure of aqueous vapour at 15° C. might be less than 12·7 mm. if the space were unsaturated, but it could not be more.

Now suppose the barometer tube were surrounded by a water-jacket through which water at different temperatures could be circulated. Say the temperature were adjusted to 30°C. Some of the surplus water in the space above the mercury would now be vaporized, until once more the space was saturated at the new temperature. The mercury would now be found to have been pushed down an additional 18·8 mm., making a total of $12 \cdot 7 + 18 \cdot 8 = 31 \cdot 5$ mm., *i.e.* the maximum pressure of aqueous vapour at 30°C. is 31·5 mm. Tables have been drawn up showing this maximum pressure over a wide range of temperatures.

Different liquids give different vapour pressures. Thus, if we were to carry out the above experiments with benzene, we should obtain a maximum pressure of 58·9 mm. at 15°C. and 120·2 mm. at 30°C.

Suppose now that when the space was saturated with water vapour at 15°C. (and the mercury had been pushed down 12·7 mm.) we were to introduce a quantity of benzene. What would happen?

The benzene would vaporize to the same extent as if no water vapour were present, finally pushing down the mercury by an extra 58·9 mm. Thus the combined pressure of the water vapour and the benzene vapour would be $12 \cdot 7 + 58 \cdot 9 = 71 \cdot 6$ mm. In this case 12·7 mm. would be spoken of as the *partial pressure* of the water vapour, and 58·9 as that of the benzene vapour. Similarly at 30°C. we should have a partial pressure of 31·5 mm. due

to water vapour and of 120·2 mm. due to benzene vapour, making a total pressure of 151·7 mm.

The case just discussed is an example of Dalton's **Law of Partial Pressures** (1801), which states that *If a space is occupied by a mixture of gases, each gas exerts the same pressure as it would exert if it occupied the whole of the space by itself.*

The commonest case in which we have to take this law into account, is when we are dealing with a volume of gas that has been collected over water. Suppose, for instance, this had been the case with the 380 c.c. of hydrogen in the example on p. 12. Then if the water is at the same level inside the containing vessel as it is outside, the *total* pressure inside is equal to that of the atmosphere (74·0 cm.). But at 12°C. the maximum pressure of aqueous vapour is 1·0 cm. Therefore, the pressure due to the dry hydrogen is $74 \cdot 0 - 1 \cdot 0 = 73 \cdot 0$ cm.,and its volume at N.T.P. would be $380 \times \frac{273}{285} \times \frac{73}{76} = \mathbf{349 \cdot 7}$ **c.c.**

Questions 9 - 11 on pp. 21 - 2 are concerned with the physical laws relating to gases.

Gay-Lussac's Law of Volumes.—The laws just reviewed (Boyle's, Charles' and Dalton's) really belong to Physics rather than to Chemistry. **Gay-Lussac's Law of Volumes,** however, deals with the volumes of gases which react chemically. *"When two gases react with one another, they do so in volumes which bear a simple ratio to one another, and to the volume of the product if the latter be a gas."*

By way of revision let us consider the following example.

A mixture of 14 *c.c. methane and* 47 *c.c oxygen was exploded. The volume of the product was* 33 *c.c., and* 19 *c.c. of this was unused oxygen, the rest being carbon dioxide. Show that we have here an example of Gay-Lussac's Law.*

We started with 47 c.c. of oxygen and 19 c.c. was not used.

∴ 47—19=28 c.c. *was* used.

Also, volume of carbon dioxide produced=33—19=14 c.c.

∴ 14 c.c. of methane has reacted with 28 c.c. of oxygen giving 14 c.c. of carbon dioxide.

These numbers (14, 28, 14) are in the simple ratio 1 : 2 : 1, as required by the law.

(Questions 12 and 13 on page 22 are of very similar type).

Avogadro's Hypothesis.—Men naturally wondered *why* there should be this simple relationship between the volumes of reacting gases, a case which specially interested them being that of hydrogen and chlorine (1 vol. of hydrogen combines with 1 vol. of chlorine giving 2 vols. of hydrogen chloride). Their first attempt at an answer was something like this: 1 *vol.* of hydrogen combines with 1 *vol.* of chlorine (experiment). But 1 *atom* of hydrogen combines with 1 *atom* of chlorine (Atomic theory).

Therefore, there must be as many atoms of hydrogen in one volume of hydrogen, as there are atoms of chlorine in an equal volume of chlorine. The idea was soon extended to include other gases, and the theory was put forward that "Equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of atoms."

It was soon shown that the statement in this form led to results which flatly contradicted the Atomic Theory. In 1811, however, Avogadro brought forward the idea of a *molecule,* and stated his famous "Hypothesis",—*Equal volumes of all gases, under the same conditions of temperature and pressure, contain equal numbers of molecules.*

In the earlier part of your course you will no doubt have worked out a number of examples based on Avogadro's Hypothesis. At this stage you might with advantage work out a few more, selecting from questions 14 - 22 at the end of this chapter.

Formulae and Equations.—To a far greater extent than most subjects, chemistry has a language of its own, —the language of formulae and equations. If we do not know the language, we cannot make much progress with the subject. If a man decided to read through a book dealing with geography or agriculture, he would be able to understand it easily enough. But he would not get

through much of an ordinary chemistry book because of the strange language in which so much of it is expressed.

If, then, we wish to become good at Chemistry, we must make ourselves thoroughly at home with equations. Let us begin with formulae, and first of all with the formulae of the common acids.

It is best to learn these, by heart, — sulphuric acid H_2SO_4; hydrochloric acid, HCl; nitric acid, HNO_3; and carbonic acid, H_2CO_3.

You will know by this time that when the hydrogen in one of these acids is replaced by a metal, a salt is produced; as, for instance, when the hydrogen of sulphuric acid is replaced by zinc (Zn) we get the salt zinc sulphate, $ZnSO_4$.

Now the three common metals, sodium (Na), potassium (K) and silver (Ag) are *univalent, i.e.* one atom of the metal replaces one atom of hydrogen, and, of course, two atoms of the metal will replace two of hydrogen. Thus, sodium sulphate will be Na_2SO_4; sodium chloride, $NaCl$; sodium nitrate, $NaNO_3$; and sodium carbonate, Na_2CO_3. The group NH_4, ammonium, behaves in the same way, ammonium chloride, for instance, being NH_4Cl, and ammonium sulphate, $(NH_4)_2SO_4$. That little list, sodium, potassium, silver, ammonium, you must learn *by heart;* you are laying up endless trouble for yourself if you do not.

Most common metals are *divalent,* one atom of the metal replacing two of hydrogen. Hence from sulphuric acid and zinc we have zinc sulphate, $ZnSO_4$; from hydrochloric acid and zinc we have zinc chloride, $ZnCl_2$, and so on. Notice carefully how the last formula is obtained. Zn is replacing 2H from hydrochloric acid HCl. To obtain 2H, we must have 2HCl, and so Zn finds itself combined with 2Cl. The writer almost apologizes for seeming to labour this point, but experience shows that King Charles's head did not appear in the famous memorial half so frequently as formulae such as Zn_2Cl appear in Chemistry answers.

There are three common trivalent metals, iron (in ferr*ic* salts; it is divalent in ferr*ous* salts), aluminium and

chromium. Ferric chloride, of course, will be $FeCl_3$, but ferric sulphate, $Fe_2(SO_4)_3$, often gives trouble. Write down iron as $Fe\equiv$ (indicating its three "valencies") and the SO_4 group as $SO_4=$ (divalent because it is combined with 2H). We have to make the number of valencies equal for the two parts of the molecule, so we have 2 $Fe\equiv$ and 3 $SO_4=$, the number for each part, of course, being six. Hence the formula $Fe_2(SO_4)_3$. You will notice that $n \times v$ is the same for the two parts of the molecule, where n is the number of atoms (or groups) and v is the valency. If you are doubtful whether you have written a formula correctly, you might very well apply this rule. If you had written Zn_2Cl, for instance, you would have $n \times v = 2 \times 2$ for the "zinc" part of the molecule, and $n \times v = 1 \times 1$ for the "chlorine" part, and you would know at once that there is something wrong.

Learn by heart the list iron, aluminium, chromium (it is the "Group III" list in analysis). You then have the common univalent metals and trivalent metals. The remainder are divalent.

The oxides of most metals have the simplest possible formulae, *e.g.* ZnO, CuO, MgO. This is because most metals are divalent, and so is oxygen (a fact easily remembered from the formula H_2O). The trivalent metals give us Fe_2O_3, Al_2O_3, and Cr_2O_3 (for iron, $n = 2$, $v = 3$; for oxygen, $n = 3$, $v = 2$; and, similarly, for the other oxides). The univalent metals would, of course, give us Na_2O, etc. but these oxides are not very common.

Hydroxides contain the group OH, *e.g.* ferric hydroxide, $Fe(OH)_3$. This hydroxide group has a valency of *one*, not three. If we write it as $-O-H$, we see that of the two oxygen valencies, one is fully engaged with the hydrogen, and so the group as a whole has only one free valency.

Sodium hydroxide then will be NaOH; calcium hydroxide, $Ca(OH)_2$, aluminium hydroxide, $Al(OH)_3$ and so on; the number of hydroxide groups being the same as the valency of the metal.

If you have carefully followed what has been said, you

will be able to write down the formulae for all common sulphates, chlorides, nitrates, carbonates, oxides (of metals), and hydroxides. You should give yourself some practice by working through exx. 23, 24 on p. 23.

And now about equations. Perhaps as you recall your previous experience with them you feel that it has not been a very successful one. That is almost entirely due to weakness in writing formulae, and there is no reason in the world why you should allow it to persist.

In writing an equation, we of course, set down on the left the formulae of the substances we use, and on the right the formulae of the substances produced, thus:—

$$\underset{\textit{Zinc}}{Zn} + \underset{\textit{Sulphuric acid}}{H_2SO_4} \rightarrow \underset{\textit{Zinc sulphate}}{ZnSO_4} + \underset{\textit{Hydrogen.}}{H_2}$$

Sometimes (as in this case), the two sides happen to balance, and there is nothing further to do.

Now consider the equation which represents the action of hydrochloric acid on calcium carbonate. Perhaps to begin with, all we can recall is that carbon dioxide is produced, so we write—

$$CaCO_3 + HCl \rightarrow CO_2 + \text{------}$$

Clearly this is very incomplete, but if our chemistry is not too bad, we shall remember that when an acid acts on a carbonate, a *salt* is produced (in this case calcium chloride, $CaCl_2$); so we get a little further—

$$CaCO_3 + HCl \rightarrow CaCl_2 + CO_2 + \text{------}$$

This does not balance, so we take 2HCl,—

$$CaCO_3 + 2HCl \rightarrow CaCl_2 + CO_2 + \text{------}$$

It is now fairly obvious that H_2O on the right will make the two sides balance, and we put it in,—all the more boldly if we remember that *base* + *acid* = *salt* + *water*, for calcium carbonate $CaCO_3$ ($= CaO \cdot CO_2$) may be regarded as a base combined with carbon dioxide.

The example just given illustrates fairly well the process of writing an equation. Strictly speaking, we cannot write it unless we know *all* the substances produced, but if everything is right except a missing H_2O, one is usually safe in putting it in (though it is extremely unorthodox to say so!).

Beyond this, guessing nearly always results in disaster. A very common mistake (and a very bad one) is for students to "balance" by putting *hydrogen* on the right-hand side. As a mere "make-weight" it is always wrong.

When you are carrying out an experiment, try to understand the general principle involved, and you will find that you can often tackle quite a hard equation. For instance, when we heat manganese dioxide with hydrochloric acid, the "general principle" is that oxygen from the manganese dioxide oxidizes (to water) the hydrogen of the acid, setting free the chlorine. The formulae are MnO_2 and HCl, and it seems reasonable to write 4HCl so as to provide enough hydrogen to combine with the oxygen. We begin, therefore,—

$$MnO_2 + 4HCl \rightarrow 2H_2O + 2Cl_2 + \quad ?$$

Shall we finish by putting Mn? Here a sort of chemical common-sense (no doubt much influenced by previous knowledge) comes to the rescue. After all, manganese dioxide does not seem much removed from a basic oxide, which would have given a salt (the chloride). This would be $MnCl_2$ (*cf.* what has been said above about the valency of metals), so we write

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2.$$

From what has been said, you will see that "rules" do not carry us very far in the writing of equations. The most important point is a knowledge of formulae. If, added to this, we understand the general principle involved, and if we know at any rate most of the substances that are produced, we shall not have much trouble with the equation; and before long we shall find ourselves quite at home with "the language of Chemistry".

Questions

N.B.—In all calculations in this book, unless alternative information is given in the question, it is to be assumed that (1) atomic weights are as given in the "approximate" column in the table (end of book), and (2) 1 litre of hydrogen at N.T.P. weighs 0·09 gm.

1. State the Law of Constant Composition, and describe an experiment by which you could illustrate it.

2. 5 gm. of copper oxide, when heated in a current of hydrogen, gave 4 gm. of copper.
   3 gm. of copper was, by suitable treatment, turned into copper oxide, and the latter was found to weigh 3·75 gm. Show that these results illustrate the Law of Constant Composition.

3. When the hydrogen of the last question was passed over 5 gm. of copper oxide (leaving 4 gm. of copper), the water produced was collected and found to weigh 1·125 gm. A quantity of water was electrolyzed and found to yield 80 c.c. of hydrogen and 40 c.c. of oxygen (oxygen is sixteen times as heavy as an equal volume of hydrogen).
   Prove that these numbers illustrate the Law of Constant Composition.

4. Zinc oxide was prepared from zinc by three different methods. By the first method, 1 gm. of zinc gave 1·246 gm. of oxide; by the second, 2 gm. gave 2·492 gm. of oxide; by the third, 3 gm. gave 3·738 gm. of oxide. Show that these numbers illustrate the Law of Constant Composition.

5. State the Law of Multiple Proportions, and describe an experiment by which you could illustrate it.
   Two oxides of an element contain respectively 22·22 per cent. and 30·00 per cent. of oxygen. Show that the law is satisfied.

6. Black oxide of mercury contains 96·15 per cent. of mercury, while the red oxide contains 92·59 per cent. Show that this statement supports the Law of Multiple Proportions.

7. Mercury forms two chlorides, one containing 15·07 per cent. of chlorine and the other 26·21 per cent. Show that these numbers are in accordance with the Law of Multiple Proportions.

8. Hydrogen was passed over 5 gm. of a certain oxide of lead to reduce it to lead, and the water produced was collected, and found to weigh 0·404 gm. The experiment was repeated with 5 gm. of a different oxide of lead, and this time 0·753 gm. of water was obtained. Show that these numbers illustrate the Law of Multiple Proportions.

   You may assume that water contains 8/9ths of its weight of oxygen, all of which is derived from the oxide of lead.

9. 1 gm. of carbon dioxide occupies 715 c.c. at 13°C. and 57 cm. pressure. Find its volume at N.T.P.

10. A quantity of oxygen measures 574 c.c. when standing over water at 14°C., and when the barometer reads 74·5 cm. Find (i) the pressure exerted by the oxygen itself (*i.e.* apart from the water

vapour), and (ii) the volume at N.T.P. (Max. pressure of aqueous vapour at 14°C. = 12 mm.).

11. 2 gm. of zinc when dissolved in hydrochloric acid was found to displace 741 c.c. of hydrogen measured over water at 16°C., the barometer reading being 75·2 cm. Find (i) the volume of the hydrogen at N.T.P. (ii) its weight, and (iii) the weight of zinc that would be required to displace 1 gm. of hydrogen. (Max. pressure of aqueous vapour at 16°C. = 14 mm.).

12. 37 c.c. of oxygen was added to 14 c.c. of carbon monoxide and the mixture was exploded. The product measured 44 c.c. of which 30 c.c. consisted of unused oxygen, the rest being carbon dioxide. Show that we have here an example of Gay-Lussac's Law.

13. A mixture of 12 c.c. methane and 53 c.c. oxygen was exploded. The volume of the product was 41 c.c., and of this 29 c.c. consisted of excess oxygen, the rest being carbon dioxide. Show that these numbers illustrate Gay-Lussac's Law.

14. The atomic weight of phosphorus is 31. At 700°C. its ~~vapour density~~ is 62. How many atoms are there in the molecule of phosphorus at this temperature? Density of gas - gm. per l.

.6. with
... to H.

15. Calculate the weight at N.T.P. of 1 litre of (*a*) acetylene (C_2H_2), (*b*) chlorine, (*c*) ammonia.

16. Calculate the weight at N.T.P. of 1 litre of air, assumed to consist of 80% nitrogen and 20% oxygen.
Which of the following gases are lighter and which are heavier than air: carbon monoxide, oxygen, sulphur dioxide, methane, hydrogen sulphide, ammonia?

17. Find the volume occupied at N.T.P. by (*a*) 7 gm. of carbon monoxide, (*b*) 32 gm. of oxygen, (*c*) 13 gm. of acetylene (C_2H_2), (*d*) 88 gm. of nitrous oxide.[1]

18. Find the weight of (*a*) 22·4 litres of carbon dioxide, (*b*) 11·2 litres of nitrogen, (*c*) 67·2 litres of methane (CH_4). The volume in each case is supposed to be measured at N.T.P.[1]

19. What volume of carbon dioxide would be obtained by the combustion of 6 gm. of carbon (*a*) if measured at N.T.P., (*b*) if the temperature were 91°C. and the pressure 80 cm.?[1]

20. What weight of mercuric oxide would be required to yield 224 c.c. of oxygen measured at N.T.P.?[1]

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[1] The gram-molecule of any gas at N.T.P. occupies 22·4 litres.

21. 30 c.c. of a mixture of hydrogen and carbon dioxide was exploded with 40 c.c. of oxygen. The final volume was 40 c.c. Find the percentage composition of the original mixture.

22. When methane is exploded with oxygen the reaction is expressed by the equation $CH_4 + 2O_2 = CO_2 + 2H_2O$. Suppose 20 c.c. of methane were exploded with 80 c.c. of oxygen, what would be the composition of the gaseous product if all volumes were measured at (*a*) 120°C., (*b*) 10°C.?

23. It is found that at standard temperature and pressure, 448 c.c. of a certain gas weighs 1·98 gm. Find its molecular weight.

24. It has been found that one volume of hydrogen combines with one volume of chlorine to form two volumes of hydrogen chloride. Hence prove that the molecule of hydrogen (and similarly the molecule of chlorine) must consist of at least two atoms. In the course of your proof you have to make a certain assumption. State clearly what it is.

25. Write the formulae for:—sodium sulphate, copper nitrate, ammonium chloride, lead carbonate, calcium chloride, silver nitrate, potassium carbonate, zinc chloride, sodium bicarbonate (=sodium hydrogen carbonate), ferrous sulphate.

26. Write the formulae for:—potassium hydroxide, ammonium nitrate, lead nitrate, ammonium hydroxide, zinc oxide, ferric oxide, sodium bisulphate, calcium hydroxide, aluminium hydroxide, ferric sulphate.

CHAPTER II

REVERSIBLE REACTIONS

If we heat chalk[1] strongly in a crucible, it decomposes intc quicklime and carbon dioxide ($CaCO_3 \rightarrow CaO + CO_2$). If, however, we expose quicklime to an atmosphere of carbon dioxide, it is soon reconverted into chalk ($CaO + CO_2 \rightarrow CaCO_3$). Chemical changes of this sort, which can take place in either direction according to conditions, are said to be ***reversible.*** They are very common, and it is important to understand certain ideas connected with them,—notably that of *equilibrium*, which we shall have occasion to discuss very shortly.

Suppose our chalk is contained in a crucible with plenty of space above it. The lid is sealed down, and the crucible will stand very high temperatures and pressures. We now heat it to, say 800°C. At this temperature chalk will decompose into quicklime and carbon dioxide, while quicklime and carbon dioxide can also re-combine to form chalk. What will actually happen when both reactions are free to take place?

For convenience of reference we shall call

$$CaCO_3 \rightarrow CaO + CO_2 \text{ ``reaction } A\text{'', and}$$

$$CaO + CO_2 \rightarrow CaCO_3 \text{ ``reaction } B\text{''.}$$

At first only reaction *A* is possible. *B* cannot take place because at this stage the necessary materials (quicklime and carbon dioxide) are not present. As soon as even a little of these substances has been produced, however, reaction *B* will set in, so that both *A* and *B* will now be in operation. But (at this early stage) *B* will not go on

[1] Not blackboard "chalk" which is calcium sulphate. In this book the term chalk = calcium carbonate.

nearly so rapidly as *A* because the necessary quicklime and carbon dioxide are present in such a low degree of concentration. As time goes on, however, these materials accumulate, with the result that *B* goes on at an ever-increasing rate, until a stage is reached at which it is going on as fast as *A*. (It cannot go on faster, because if it did there would be a reduction in the supply of quicklime and carbon dioxide, and reaction *B* would automatically slow down.)

From this time forward, if it were possible to make analyses of the contents of the crucible at intervals of, say, five minutes, we should find no change whatever in the quantities of the three substances present, *not* because no chemical change is taking place, but because *two opposite chemical changes are going on at equal rates.* Such a condition of things is known as a state of ***chemical equilibrium.*** This will be maintained so long as the conditions (temperature, for instance) remain unchanged.

Bluestone and Other Hydrates.—An interesting type of reversible reaction is illustrated by the substance, bluestone. This has the formula $CuSO_4 . 5H_2O$. (Its proper name would be "copper sulphate pentahydrate", substances which contain water of crystallization being known as *hydrates.*)

Suppose we make a mercury barometer as indicated on p. 13 and let a crystal of bluestone float to the top of the mercury. A reversible reaction at once sets in, represented by the equation $CuSO_4 . 5H_2O \rightleftarrows CuSO_4 + 5H_2O$.[1] This is exactly comparable with the reaction we have just studied, and which might, in fact, have been written $CaO . CO_2 \rightleftarrows CaO + CO_2$. We shall, therefore, not follow the story out in detail, though it would be a very good exercise for the student to do so for himself. In this case equilibrium is indicated by the fact that the mercury is

[1] Strictly speaking, an intermediate hydrate $CuSO_4 . 3H_2O$ is produced, but our main concern at this stage is to get a firm grip of general principles.

pushed down by a definite amount (4 mm. at 15°C.), showing that the amount of water present as vapour is constant.

Notice that if in the atmosphere surrounding the bluestone, the pressure of aqueous vapour is as great as 4 mm., the bluestone does not (on balance) lose any water. That is why under ordinary atmospheric conditions, this substance remains fully hydrated.

Some hydrated salts (Glauber's salt, for instance, $Na_2SO_4 . 10H_2O$) have at ordinary temperatures a vapour pressure *greater* than that usually found in the atmosphere. On free exposure to the air such substances ***effloresce***, *i.e.* they spontaneously lose their water of crystallization. Another common example is washing soda, $Na_2CO_3 . 10H_2O$. It happens in this case, however, that a lower hydrate exists ($Na_2CO_3 . H_2O$), which has a vapour pressure less than that usually existing in the atmosphere, so dehydration does not proceed beyond the "monohydrate" stage.

The case of calcium chloride, $CaCl_2 . 2H_2O$, is in some respects of opposite character. Its vapour tension is very low,—much lower than that existing in the atmosphere,—but a higher hydrate also exists ($CaCl_2 . 6H_2O$), whose vapour tension is much greater than that of $CaCl_2 . 2H_2O$. Hence, on exposure to the atmosphere, the lower hydrate readily takes up moisture becoming $CaCl_2 . 6H_2O$. For the same reason, the lower hydrate is much used in the drying of gases.

Gladstone's Experiment.—An interesting experiment on the subject of reversible reactions, first carried out in 1855 by J. H. Gladstone, is based on the fact that ferric chloride reacts with ammonium thiocyanate giving an intensely red solution of ferric thiocyanate. The equation is actually

$$FeCl_3 + 3NH_4CNS \rightleftarrows Fe(CNS)_3 + 3NH_4Cl$$

but as this is rather ponderous, we shall for convenient reference write it as $FC + AT \rightleftarrows FT + AC.$

First notice *why* we get equilibrium. At the beginning, the only possible reaction is that from left to right, because

no ferric thiocyanate (FT) and ammonium chloride (AC) have yet been produced. As time goes on, however,

(i) FC and AT become reduced in concentration, and the left-to-right reaction slows down;

(ii) FT and AC increase in concentration and the right-to-left reaction speeds up. Ultimately,—and in this case "ultimately" means only a fraction of a second,—a stage is reached at which both reactions go on at the same rate, *i.e.* equilibrium is established.

What will happen if to this system in equilibrium we add a more concentrated solution of ferric chloride than before?

Collisions between AT molecules and FC molecules will now be more frequent, and the left-to-right reaction will be speeded up. For the moment equilibrium will be upset. This very speeding up will result, however, in an increased concentration of FT and AC molecules (which are now being produced at a greater rate), and, therefore, there will be an increase in the speed of the right-to-left reaction, until in time (a very short time in this particular case) equilibrium is once more restored. In this new state of equilibrium the concentration of FT and AC will evidently be greater than it was before, and as ferric thiocyanate (FT) has a marked red colour, we should be able to detect this increased concentration.

To test our conclusion, fill four gas-jars *P,Q,R,S* about three parts full of water, about 250 c.c. in each. Prepare a solution of ferric chloride containing about 8 gm. per litre and one of ammonium thiocyanate containing about 12 gm. per litre. Add 10 c.c. of each to the water in each of the jars *P,Q,R,S*. This will give a sort of golden brown colour. Stir. Now, keeping *P* as a colour standard, add some more of the ferric chloride to *Q*. The colour is deepened as we had anticipated.

Addition of a stronger solution of AT should obviously have a similar effect (because once again, collisions between AT molecules and FC molecules would be more frequent). On the other hand, addition of a stronger solution of AC would cause an increased number of FT molecules to

be used up, and the solution should become paler. To test these conclusions, add some of the ammonium thiocyanate solution to *R*. Once more the colour is deepened. Now add some of the ammonium chloride solution to *S*. The colour becomes paler than the standard.

Other Cases of Equilibrium.—The idea of equilibrium is by no means confined to chemical action, nor even to what would generally be called "science" (*cf.* question 3 at the end of this chapter). Examples are often met with in the study of Physics. For instance, when we allow a little water to float on the top of mercury in a barometer (*cf.* p. 13), the *constant* vapour pressure is the result of equilibrium between the rate at which water turns into vapour, and that at which vapour condenses to water. If for water vapour we substitute ice, we have another example, though here the pressure is very low (about 4·5 mm. at 0°C.). You should try to work out these cases in greater detail for yourself.

Another example of what we may call physical equilibrium occurs in connection with saturated solutions. We stir up common salt (for instance) with water. More and more dissolves until the solution is saturated. At this point, though we may add more salt and stir vigorously, no more will dissolve,—the surplus simply lies at the bottom of the beaker. Really a state of equilibrium has been reached, in which molecules of salt present in the solution are falling back on the solid at the same rate as molecules from the solid are entering the solution.

According to this, the solid at the bottom would not be always the *same* solid, though it is constant in amount. Have we any evidence of such change?

It so happens that we have. It has been found that if the solid in equilibrium with its saturated solution consists of very small crystals, the latter gradually become *larger* (and, of course, correspondingly fewer). Further, irregularities in the crystals, such as chipped surfaces, tend to disappear.

Prevention of Reverse Action.—Returning now to cases of chemical equilibrium, we may notice that in many instances the reverse action is not desired. A lime-burner, for instance, is interested in the *direct* action $CaCO_3 \rightarrow CaO + CO_2$, but he certainly does not want his work undone by carbon dioxide combining with quick-lime. He prevents the reverse action very simply, by arranging for a good draught, so that carbon dioxide shall be carried away as fast as it is produced. The method of the lime-burner,—removal as fast as it is produced of at least one of the products of the direct action,—is one of the commonest and best methods of causing the direct action to "go to completion".

We cannot make the action of ammonium thiocyanate on ferric chloride proceed to completion, because we have no means of removing either of the products of the reaction (ferric thiocyanate and ammonium chloride). The trouble is that they are both soluble. On the other hand, consider the action $AgNO_3 + NaCl \rightarrow AgCl + NaNO_3$, which represents what happens when we add a solution of silver nitrate to one of sodium chloride. In this case, the silver chloride produced is insoluble, and is, therefore, incapable of reacting with the sodium nitrate; so there is no question of a reverse action. For practical purposes the silver chloride is "removed" as fast as it is formed. A very large number of reactions between solutions are non-reversible for the same reason.

Mass Action.—Suppose we pour dilute hydrochloric acid on a strip of zinc contained in a beaker. Hydrogen begins to come off at a rate which (after the first few seconds) is fairly steady. If, now, we add a little *concentrated* acid, the rate is definitely increased. The reason is pretty obvious. There are now more molecules of hydrogen chloride present per c.c. than before, and so collisions between acid molecules and zinc molecules are more frequent. Notice that it is *concentration* that matters, not mere quantity. A strip of zinc immersed in a

beaker half-full of dilute acid would cause hydrogen to be given off just as fast as if the beaker were full (of acid of the same strength). Similarly, a glowing splint glows just as brightly in a small gas-jar full of air as in a large one. If, however, we transfer the splint to a jar of oxygen, there is an immediate increase of activity, simply because the oxygen molecules are more *concentrated,* and for every molecule that collided with the splint in the first instance, there are now about five. The effect thus produced by increasing the concentration of one of the materials is known as ***mass action.*** The term is not a particularly good one, because it suggests that the rate of chemical action depends simply on the mass of material present, but as we have just seen, it really depends on the concentration.

The principle of mass action applies, of course, to *each* of the actions constituting a reversible reaction. In our thiocyanate experiment, for instance, we were able to stimulate the direct action by increasing the concentration of either the ammonium thiocyanate or the ferric chloride, while we were able to stimulate the reverse action by increasing the concentration of the ammonium chloride. The constant removal of carbon dioxide to prevent the reversal of the action $CaCO_3 \rightarrow CaO + CO_2$ may also be regarded as an extreme example of mass action, the concentration of the carbon dioxide in this case being reduced to zero.

Le Chatelier's Law.—Let us now go back for a little while to the first case we studied,—chalk in equilibrium with quicklime and carbon dioxide ($CaCO_3 \rightleftarrows CaO + CO_2$), at a temperature which we supposed to be 800°C. What would happen if the temperature were raised to 1000°C.?

Both the direct action (decomposition of chalk) and the reverse one would be speeded up, but the direct one to a greater extent. As a result, equilibrium would be disturbed for a time, carbon dioxide and chalk being produced at a greater rate than they can recombine. The

very fact, however, that these substances are increasing in quantity (in a space of constant volume), causes a speeding up of the reverse reaction, until by and by a new state of equilibrium is attained,—*new*, because there would be less chalk, and more quicklime and carbon dioxide, than was the case at 800°C.

Now the decomposition of chalk absorbs heat, and is, therefore, a process which tends to bring about a reduction of temperature. Hence, we may sum up the situation by saying that (i) we had a system in equilibrium, (ii) we *increased* the temperature, and (iii) equilibrium was displaced in such a way as tended to bring about a *reduction* of temperature.

Let us next reconsider the ammonium thiocyanate reaction from a somewhat similar point of view. We represented it as $FC + AT \rightleftarrows FT + AC$. By *increasing* the concentration of ferric chloride (FC) we stimulated the left-to-right reaction, and as we saw, a new state of equilibrium was established. In the process some FC and AT molecules were used up. In this case, then, (i) we had a system in equilibrium, (ii) we *increased* the concentration of one of the reacting substances, and (iii) equilibrium was displaced in such a way as tended to *reduce* this concentration.

The cases just considered are examples of **Le Chatelier's Law**, which states: *If a system is in equilibrium under certain conditions of temperature, pressure, or concentration, and one or more of these is altered, then the equilibrium will be displaced in such a way as will tend to restore the original conditions.*[1]

You should work out for yourself the application of this law to the other cases of equilibrium which have been considered in the present chapter.

Practical Applications.—Reversible reactions are very frequently met with in industrial chemistry, and by a

[1] Not inaptly, one writer has nicknamed this "The Law of Pure Cussedness".

proper understanding of the principles involved, chemists are able to advise as to how a large-scale process can best be carried out. By way of illustration, we shall take the manufacture of ammonia from nitrogen and hydrogen. Some details will be given on pp. 137-8. The point we are here concerned with is that the reaction involved is a highly reversible one ($N_2 + 3H_2 \rightleftarrows 2NH_3$), and we want to know what conditions will give us the best possible yield of ammonia.

(i) Shall we work at a high pressure or a low one?

The above equation shows that when nitrogen combines with hydrogen there is a decrease in the number of molecules, and, therefore, in the pressure. If we work at a higher pressure, Le Chatelier's Law tells us that equilibrium will be displaced in such as way as will tend to *reduce* the pressure, *i.e.* more nitrogen will combine with hydrogen, which is what we want. Hence in the making of ammonia by this process, manufacturers work at the highest possible pressure.

(ii) Shall we work at a high temperature or a low one?

Ammonia like most compounds is *exothermic, i.e.* when it is formed from its elements, heat is given out (and the temperature, therefore, increased) while, when it is decomposed, heat is taken in (temperature decreased). Now we want the equilibrium mixture to contain as high a percentage of ammonia as possible, a state of things which tends to produce *high* temperature. It seems, then, that the process ought to be worked at as *low* a temperature as possible, but

(iii) at low temperatures chemical actions take place slowly. Nitrogen combines with hydrogen only slowly to form ammonia, and the reverse action is also slow. Hence, although at low temperatures the equilibrium mixture would contain a high percentage of ammonia, it would take a long time for equilibrium to be established. It might easily take weeks!

Evidently the best course would be to work at a low temperature if only we could somehow, at the same time,

make the reactions take place with reasonable speed. Now a suitable catalyst will speed up chemical actions, and so one is always employed in the production of synthetic ammonia. Even with the help of a catalyst, however, it is found that equilibrium takes too long to be established if the temperature is much below 600°C. Taking everything into consideration then, it is found best

(i) to work at the highest possible pressures,

(ii) to work at as low a temperature as is consistent with the rapid attainment of equilibrium,

(iii) to employ a catalyst, which makes it possible for the temperature in (ii) to be much lower than it otherwise would be.

Thus, by a proper understanding of the underlying theory, chemists have found it possible to base a highly successful industrial process on what appeared to be a very unpromising reversible reaction.

Questions

1. Mention three reversible reactions you have met with, other than those referred to in this chapter.

2. Suppose that when a condition of equilibrium existed in the sealed crucible considered on p. 24, an additional amount of carbon dioxide were somehow introduced. Trace out what would happen.

3. Apply your general ideas on the subject of equilibrium to explain the following facts:—

(i) It may be impossible to boil a large kettle of water by means of a single bunsen burner, no matter how much time is available.

(ii) A boy pumping up a bicycle tire containing a small puncture finds that it reaches a stage when it ceases to go harder, in spite of continued steady pumping.

4. When doing analysis, you find that on adding a solution of bismuth chloride to water, a white precipitate of the oxychloride is produced ($BiCl_3 + H_2O \rightleftarrows BiOCl + 2HCl$). On adding a little hydrochloric acid to the milky liquid, it at once becomes clear, and on adding much water to the clear liquid it again becomes milky. Explain.

5. Chlorine reacts with water thus:—$Cl_2 + H_2O \rightleftarrows HCl + HClO$ (hypochlorous acid). In the presence of sunlight, hypochlorous acid is readily decomposed ($2HClO \rightarrow 2HCl + O_2$).
(*a*) How would you arrange to bring the reaction between chlorine and water to completion?
(*b*) Suggest a means of preserving a solution of chlorine in water.

6. Some small crystals of bluestone are kept in a desiccator containing sulphuric acid. After a few weeks they are found to have turned white. Why?

7. Use Le Chatelier's law to explain why a solid is usually more soluble in hot water than in cold, while a gas is less soluble. (*Hint.*—When a solid dissolves in water there is usually a fall of temperature; when a gas dissolves there is a rise.)

8. One process for the "fixation" of atmospheric nitrogen is based on the reaction $N_2 + O_2 \rightleftarrows 2NO$. The highest possible temperature is employed (electric arc). Why? (*Hint.*—Nitric oxide is an endothermic compound, *i.e.* when it is formed from its elements, heat is absorbed.)

CHAPTER III

FREEZING POINT, BOILING POINT, and MOLECULAR WEIGHT

PURE water freezes at 0°C. If sugar is dissolved in it, it freezes at a lower temperature, and experiment soon shows that the more concentrated we make the solution the more is the freezing point depressed. This is probably what we should expect.

For *dilute* solutions, the depression of the freezing point is actually *proportional* to the amount of sugar dissolved (Blagden's Law). Suppose, for instance, that we take three beakers each containing 100 gm. of water, and in the first we dissolve 5 gm. of cane sugar, in the second 10 gm. and in the third 15 gm. Using a very sensitive thermometer it is found that the first solution freezes at —0 · 27°C., the second at —0 · 54°C. and the third at —0 · 81°C. The depressions then are 0 · 27°, 0 · 54° and 0 · 81° and these are in the ratio 1 : 2 : 3.

Other substances besides sugar depress the freezing point, but the amount of the depression depends on the substance dissolved. For instance, if in 100 gm. of water we dissolve 5 gm. of a crystalline substance known as urea, the freezing point would be depressed by 1· 55° (about six times the depression produced by 5 gm. of sugar). A very

FIG. 3.

interesting connection has been found between the molecular weight of the solute (*i.e.* the substance dissolved) and the depression of freezing point which it produces. Suppose we have three beakers each containing 100 gm. of water. In the first we dissolve 34·2 gm. cane sugar, in the second 6 gm. urea, and in the third 3·4 gm. hydrogen peroxide. The molecular weights of these substances are respectively 342, 60, and 34 and the quantities mentioned are one-tenth of the respective gram-molecules.[1]

It is now found that the freezing point of each solution is the same (—1·86°C.). This is an example of a law discovered in 1883 by Raoult, *viz. If in equal quantities of a solvent we dissolve different substances (other than acids, bases and salts)*[2] *in quantities proportional to their molecular weights, the solutions thus obtained will all have the same freezing point.*

In the case of water, the depression produced by dissolving 1 gram-molecule of the solute in 1000 gm. is found to be 1·86°C., and this number 1·86 is known as the **molecular depression of freezing point** for water.

The solvent used need not be water, but the molecular depression depends upon the solvent. Thus for benzene it is 4·9 and for acetic acid 3·9.

Alternative statement.—Before passing on, it is well worth noting that both Blagden's Law and Raoult's Law are included in the following statement: — *If a liquid has a substance dissolved in it, its freezing point will be depressed by an amount proportional to the number of molecules (or ions)*[2] *of the solute.*

That this statement includes Blagden's Law is obvious enough. With regard to Raoult's, we notice that when we dissolve "different substances in quantities proportional to their molecular weights", we are taking equal numbers

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[1] The gram-molecule is the number of grams corresponding to the molecular weight; *e.g.* the molecular weight of hydrogen peroxide, H_2O_2, is $2 + 32 = 34$; therefore, the gram-molecule is 34 gm.

[2] This point was *not* expressed in Raoult's original statement; its significance will appear later (pp. 43ff.).

of molecules of the different substances, and so it must be true that these equal numbers produce equal depression.

The form of the statement just given will be very useful when we come to study Ionization in the next chapter.

Determination of Molecular Weight. — Since there is such a definite connection between freezing point and molecular weight, we can evidently find the latter by a freezing-point method. Suppose, for instance, that we wish to find the molecular weight of some substance X. We could take 1 litre of water (1000 gm.) and by repeated trials find how many grams of X we must dissolve in it in order that the freezing point may be $-1 \cdot 86°C$. This number is the molecular weight.

There is no need, however, for these repeated trials. Provided the weight of water and the weight of X are known, we can easily calculate the molecular weight as in the following example.

$0 \cdot 4$ *gm. of fructose was dissolved in* 20 *gm. of water, and the solution was found to freeze at* $-0 \cdot 207°C$. *Find the molecular weight of fructose to the nearest whole number (molecular depression for water* $= 1 \cdot 86$).

Let m = required molecular weight.

Then m gm. fructose in 1000 gm. water gives depression of $1 \cdot 86°$.

$\therefore$ m gm. fructose in 20 gm. water gives depression of $1 \cdot 86 \times \frac{1000}{20}$,

(because the solution is *stronger* in the ratio of 1000 : 20).

$\therefore$ $0 \cdot 4$ gm. fructose in 20 gm. water gives depression of

$$1 \cdot 86 \times \frac{1000}{20} \times \frac{\cdot 4}{m}.$$

But this depression $= 0 \cdot 207°$ (given).

$$\therefore \quad 1 \cdot 86 \times \frac{1000}{20} \times \frac{\cdot 4}{m} = 0 \cdot 207.$$

Solving the equation, we get $m = 180$.

The thermometer used in freezing-point determinations is, of course, of quite a special type. The bulb is very large and the bore of the tube very fine. Thus a small increase

of temperature causes the mercury to rise a long way and indeed the whole stem is divided to show only 6 degrees. The space indicating 1 degree is so large that with the help of a lens, readings may be taken to the one-thousandth of a degree centigrade.

Fig. 4.—Beckmann thermometer.

It should be noticed that there is no need for the thermometer to record the *actual* freezing point, but only the *difference* between the freezing point of the pure solvent and that of the solution. Hence we begin by adjusting the height of the mercury in the stem, either shaking some out into the little reservoir at the top, or introducing more from the same store, as may be required.

Elevation of Boiling Point. — When sugar, urea, etc. are dissolved in water, the latter not only freezes at a lower temperature than 0°C., but it also boils at a higher temperature than 100°C. Laws similar to those we have just been considering hold good in the case of boiling point, *i.e.*:

(1) For a given dissolved substance, the elevation of boiling point is proportional to the concentration of the solution.

(2) If in equal quantities of a solvent we dissolve different non-volatile substances in quantities proportional to their molecular weights, the solutions thus obtained will all have the same boiling point.

Corresponding to the molecular depression of freezing point, we have the **molecular elevation of boiling point.** In the case of water this is 0·52, *i.e.* if in 1 kilogram of water we dissolve 1 gram-molecule of a solute, the boiling point will be 100·52°C. instead of 100°C. Let us now work through the following example:—

"In 1890 E. Beckmann found that when 1·4475 *gm. of phosphorus was dissolved in* 54·65 *gm. of carbon disulphide, the boiling point was raised by* 0·486°. *Calculate the molecular weight of phosphorus. Given that the atomic weight is* 31, *what conclusion can be drawn from your answer? (Molecular elevation for carbon disulphide* = 2·35.)

Let m = required molecular weight.

Then m gm. of phosphorus in 1000 gm. of carbon disulphide raises the boiling point by 2·35°.

$\therefore$ m gm. in 54·65 gm. raises b.p. by $2{\cdot}35 \times \frac{1000}{54{\cdot}65}$.

$\therefore$ 1·4475 gm. in 54·65 gm. raises b.p. by $2 \cdot 35 \times \frac{1000}{54 \cdot 65} \times \frac{1{\cdot}4475}{m}$.

But b.p. is raised by 0·486° (given).

$$\therefore\ 2{\cdot}35 \times \frac{1000}{54{\cdot}65} \times \frac{1.4475}{m} = 0{\cdot}486.$$

Solving, we get $m = 128{\cdot}2$.

This is approximately 4 times the atomic weight (31), so we conclude that the molecule of phosphorus contains 4 atoms,—at any rate when it is dissolved in carbon disulphide.

It will already have been shown that from the percentage composition of a substance we can work out its simplest (or " empirical ") formula, but that this is not necessarily the true or molecular formula. To determine the latter, we must know the molecular weight (in addition to the percentage composition). Hitherto we have only been able to find the molecular weight of substances that could be vaporized without decomposition, but we can now include any substance[1] for which we can find a suitable solvent. For example,—

A substance is found to have the percentage composition, carbon 65·4, *hydrogen* 5·5, *oxygen* 29·1. *A solution of* 0·28 *gm. of the substance in* 15 *gm. of water was found to freeze at* —0·317 *C. Find the molecular formula of the substance (molecular depression for water* = 1·86).

[1] Provided it does not ionize; see Chapter IV.

We first find the simplest formula.

Elements	Percentage	These numbers are proportional to	If 1 = H
Carbon	65·4	$65{\cdot}4 \times \frac{12}{65{\cdot}4} = 12$	12 = C
Hydrogen	5·5	$5{\cdot}5 \times \frac{12}{65{\cdot}4} = 1$	1 = H
Oxygen	29·1	$29{\cdot}1 \times \frac{12}{65{\cdot}4} = 5{\cdot}33$	5·33 = ⅓ O

From $CHO_{1/3}$ we derive the simplest formula C_3H_3O.

We now proceed to find the molecular weight. If this = *m*, we have *m* gm. in 1000 gm. water gives depression of 1·86.

$\therefore$ ·28 gm. in 15 gm. water gives depression of $1{\cdot}86 \times \frac{{\cdot}28}{m} \times \frac{1000}{15}$.

$$\therefore\ 1{\cdot}86 \times \frac{{\cdot}28}{m} \times \frac{1000}{15} = {\cdot}312 \text{ (the observed depression).}$$

Solving, we get $m = 113$.

Now the molecular weight of C_3H_3O would be $36 + 3 + 16 = 55$, and our value for *m* is approximately twice this. The molecular formula is therefore $C_6H_6O_2$.

As indicated in the last example, the degree of accuracy obtainable by the freezing-point (or boiling-point) method is not very great, but it is quite sufficient to enable us to decide which multiple of the empirical formula we must select; and in most cases nothing else is required.

Questions

1. To protect fruit and vegetables from damage during (not too severe) frosty weather, a large bowl of water is sometimes placed in the storeroom, cellar, etc., where they are kept. Explain the action.

2. 5 gm. of cane-sugar ($C_{12}H_{22}O_{11}$) is dissolved in 150 c.c. of water, and the feezing point of the solution in found to be lowered by 0·177°C. What value does this give for the molecular weight of the sugar? What value do you calculate from the formula?

3. W. Orndorff and J. White in 1893 found that by dissolving 0·2735 gm. of hydrogen peroxide in 19·86 gm. of water, the freezing point was depressed by 0·746°. Calculate the molecular weight of hydrogen peroxide.

4. In 1889 W. Tammann found that when he dissolved 0·022 gm. of sodium in 100 gm. of mercury, the freezing point of the latter was lowered by 0·39°C. Calculate the molecular weight of sodium. What conclusion do you draw as to the number of atoms in the molecule of sodium, when it is dissolved in mercury? (Molecular depression for mercury = 42·5.)

5. Assuming that a two-metal alloy consists of a solution of each metal in the other, how would you expect its melting point to compare with those of its constituents.

6. It is said that vegetables can be cooked more rapidly if a generous amount of salt is added to the water in which they are boiled. How do you account for this?

7. When 0·36 gm. of urea, $CO(NH_2)_2$, was dissolved in 15 gm. of water, the boiling point of the latter was raised by 0·201°C. Calculate the molecular weight, and compare it with the value obtained from the formula. (Molecular elevation for water = 0·52.)

8. In 1890 E. Beckman found that by dissolving 2·0579 gm. of iodine in 30·14 gm. of ether, the boiling point of the latter was raised by 0·566°C. Calculate the molecular weight of iodine, and comment on the result obtained. (Molecular elevation for ether = 2·16.)

9. A certain hydrocarbon is found to contain 6·25 per cent. of hydrogen. Calculate its simplest formula. When 0·618 gm. of it was dissolved in 14 gm. of carbon disulphide, the boiling point of the latter was raised by 0·784°. Calculate the molecular weight, and (using your previous result) the molecular formula. Molecular elevation for carbon disulphide = 2·37.

CHAPTER IV

IONIZATION

It may have struck the student that the substances which we used in the experiments of last chapter were rather unusual ones,—urea, for instance. The reason for this will appear presently.

Let us now take a much commoner substance,—sodium chloride. The molecular weight of NaCl is $23 + 35 \cdot 5 = 58 \cdot 5$, so if we dissolve 58·5 gm. in 1 litre of water we should expect the solution to freeze at —1·86°C. Actually we find that the freezing point instead of being depressed by 1·86 degrees, is depressed by nearly[1] *twice* this amount. If the case of sodium chloride stood alone, we should no doubt regard it as a very curious exception to Raoult's law and leave it at that. But this double depression (or approximately double) is also shown by potassium bromide (KBr), sodium nitrate ($NaNO_3$), and scores of other salts; while calcium chloride ($CaCl_2$), magnesium chloride ($MgCl_2$), and many other salts actually show three times the theoretical depression. Similar deviations are also shown in the elevation of boiling point, *i.e.*, salts which show a double (or treble) depression of the freezing point also show a double (or treble) elevation of the boiling point.

For the present we shall confine ourselves to the case of sodium chloride. No doubt if the mystery can be cleared up in this case, the same explanation will apply to the other cases also.

Certain results connected with electricity seem likely to have an important bearing on the subject. Suppose we

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[1] See pp. 45-6.

have an electric circuit which includes two platinum plates A and B. Except for the gap between A and B, a current would flow. If A and B are placed in a solution of common salt the current *does* flow. If they are placed in a solution of cane-sugar it does not. Many other experiments have been tried, using the same apparatus but different solutions, and the results may be summed up in the following statements.

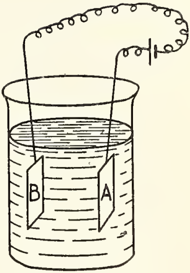

Fig. 5.

Substances which in solution produce excessive depression of freezing point and elevation of boiling point, are electrolytes (i.e., when dissolved they will convey an electric current).

Substances which in solution produce depression of freezing point and elevation of boiling point in accordance with Raoult's law are non-electrolytes.

A Swedish chemist, named Svante Arrhenius, pondered long over the state of things summarized in the last few lines. Could it be, he asked himself, that there is something *electrical* in the make-up of a substance like sodium chloride?

The result of his thought was the **Ionization Theory**, which is briefly as follows. The molecule of an acid, a base, or a salt consists of two parts, one carrying one or more positive and the other one or more negative electric charges, so that the molecule as a whole is electrically neutral. The molecule of sodium chloride, for instance, NaCl, consists of a positively-charged sodium atom combined with a negatively-charged chlorine atom.

When such a substance is dissolved in water, the two portions separate. According to this, a solution of sodium chloride contains positively-charged sodium atoms and negatively-charged chlorine atoms, moving about indepen-

dently of one another. They are known as *ions* (Gr.= *wanderers*), and their production from the original molecule is known as **ionization.**

Before proceeding further, let us deal with what seems to be a serious objection. If a solution of sodium chloride contains the separate atoms, would it not smell of chlorine? And would not the sodium present act vigorously upon the water?

The answer is that sodium atoms in the ordinary sense are *not* present, but sodium atoms each carrying an electric charge. We have, in fact, a sort of compound of sodium and electricity, whose properties differ entirely from those of sodium, much as a compound of hydrogen and oxygen (water) has properties differing entirely from those of hydrogen. Similarly, the properties of chlorine *ion* are very different from those of chlorine.

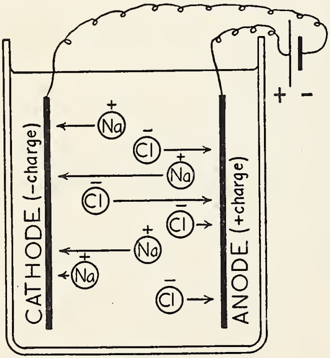

Fig. 6.—Movement of ions.

If into such a solution we introduce two metal plates, one positively-charged by being connected with the positive plate of a battery, and the other negatively charged, then the positive plate attracts the chlorine ions according to the well-known law that unlike electric charges attract one another. On touching the plate the chlorine atoms are discharged, their negative charge neutralizing, so to speak, a corresponding amount of the positive charge on the plate. This loss of positive charge is made good by a renewed flow from the battery, and as the neutralizing action is continuous, the flow from the battery is also continuous. Quite similar remarks apply to the negative terminal, except

that here it is a case of a negative charge being continuously neutralized by the positively-charged ions.

Evidently the ionization theory, which we have just been considering, accounts simply enough for the experimental fact that certain solutions "conduct" the electric current. We must now notice what happens to the ions. On being discharged, each chlorine ion becomes an ordinary chlorine *atom,* and behaves as such. Near the anode (as the positive plate is called), the solution begins to smell of chlorine, and will bleach litmus paper. Similarly, at the cathode (negative plate) ordinary sodium atoms are formed by the discharge of the ions. We should not expect sodium to collect on the cathode, because water is present. It reacts with the water, producing sodium hydroxide and hydrogen ($2Na + 2H_2O \rightarrow 2NaOH + H_2$).

The process just described is known as **electrolysis**, and later on we shall come across several other examples of it. For the present, our main business is to realize that the *facts* of electrolysis are in harmony with the *theory* of ionization put forward by Arrhenius.

But other facts are also explained by this theory. When sodium chloride dissolves in water, separating into ions, there are present twice as many "particles" (let us call them) as there would have been if the molecule had remained undivided. This would account for the double depression of freezing point and elevation of boiling point. (If this is not clear, refer back to the "Alternative Statement" on page 36). In the same way, each molecule of calcium chloride ($CaCl_2$) would give rise to *three* ions, Ca, Cl, and Cl, and this would account for the three-fold depression (and elevation).

We might notice here that sodium chloride (for instance) in solution does not give *quite* twice the depression that would be expected from Raoult's law. A solution containing one-tenth of a gram-molecule per litre, if it obeyed the law, would show a depression of 0·186°C., and if every molecule split up into two ions, we should expect a depression of $2 \times 0{\cdot}186 = 0{\cdot}372°$. The depression actually

observed is only 0·342°. The explanation is that not *all* the sodium chloride is ionized, and, therefore, not quite twice as many "particles" are present as in the case of the un-ionized salt. In fact, we are really concerned with a reversible reaction, which would be expressed as $NaCl \rightleftharpoons Na^{+} + Cl^{-}$ (Na^{+} means a sodium ion, the "plus" standing for the positive charge; similarly Cl^{-} stands for a chlorine ion, *i.e.* a chlorine atom carrying a negative charge).

The ionization of calcium chloride would be expressed as $CaCl_2 \rightleftharpoons Ca^{++} + 2Cl^{-}$. Ca^{++} indicates that the calcium atom carries *two* units of positive charge. If it did not, the molecule as a whole would not be neutral.

Some Practical Consequences.—The fact that ionization is a kind of reversible reaction has many practical consequences, and it will be interesting to follow out one or two of them.

Consider a saturated solution of barium chloride in a beaker, with some of the undissolved salt at the bottom. In Chapter II, we saw that we have here a case of equilibrium, molecules of the solid escaping into the solution at the same rate as molecules of the dissolved substance are being deposited at the bottom. We may write

$$BaCl_2 \text{ (solid)} \rightleftharpoons BaCl_2 \text{ (dissolved)} \qquad \text{(i)}$$

But the molecules in solution are also giving rise to ions at the same rate as the ions are re-combining to form molecules, so we write $BaCl_2 \text{ (dissolved)} \rightleftharpoons Ba^{++} + 2Cl^{-}$ (ii)

Suppose now we add a quantity of strong hydrochloric acid. This ionizes freely, and there is a great increase in the *concentration* of chloride ion in the solution. The result is that barium ions come into contact with chloride ions much more frequently, and, therefore, the number of barium chloride molecules in the solution tends to increase.

But that number is already as great as it can be, for we are dealing with a *saturated* solution. Therefore, as an increased number of molecules is formed from the ions, the molecules already in solution are deposited as solid. Considering the chain of equilibria

$$BaCl_2 \text{ (solid)} \rightleftarrows BaCl_2 \text{ (dissolved)} \rightleftarrows Ba^{++} + 2Cl^{-}$$

we say that in both cases "the equilibrium is displaced to the left".

The conclusion at which we have just arrived is easily put to the test. We have only to prepare a saturated solution of barium chloride in a test-tube and add a little concentrated hydrochloric acid, when a fine crystalline precipitate of barium chloride is at once obtained. Sodium chloride is easily precipitated in the same way.

Notice that a mere increase in the *number* of chloride ions would not be sufficient; there must be an increase in the *concentration.* The acid added must be so strong that in spite of the increase in volume (which of itself would give the ions more space in which to move about) there are more chloride ions per c.c. than there were before.

Another interesting result conected with a reaction between ions is observed when we dissolve cupric chloride in water. A concentrated solution is green, but when this is diluted with water it becomes blue. If when the solution has been just sufficiently diluted to turn blue, we add a little concentrated hydrochloric acid, it again turns green. What is the reason for these curious colour changes?

Anhydrous cupric chloride is really yellow. When we dissolve it in water ionization takes place in accordance with the equation $CuCl_2 \rightleftarrows Cu^{++} + 2Cl^{-}$. Now in concentrated solution only a little of the salt is ionized, because the ions are so closely packed together that the tendency to recombine into molecules is very strong. Thus, so far as colour is concerned, a concentrated solution contains (i) the actual *molecules,* which are yellow, and (ii) a number of cupric *ions* which are blue (chloride ions too, but these are colourless). The blue and yellow, of course, give green.

When the solution is diluted, the equilibrium $CuCl_2 \rightleftarrows Cu^{++} + 2Cl^{-}$ is displaced to the right, *i.e.* ionization takes place much more freely. The molecules are now too few to contribute an appreciable amount of yellow, and the colour observed is simply the blue due to copper ion.

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The addition of hydrochloric acid increases the concentration of chloride ion, and this, of course, displaces the equilibrium to the left. Hence the yellow constituent due to the molecules again becomes prominent.

Summing Up the Evidence.—At this point let us sum up the evidence, as far as we have considered it, in favour of Arrhenius' theory of Ionization.

(1) If a substance really ionizes in solution, it would give a greater number of particles than if its molecules had remained undivided. We might, therefore, expect a correspondingly greater depression of freezing point, and elevation of boiling point. This is found to be the case.

(2) We ought to find that solutions which give this greater depression of freezing point, etc., will convey the electric current, and vice versa. This is again the case.

(3) The same theory furnishes a simple explanation of such facts as the precipitation of barium chloride by means of hydrochloric acid, and the colour changes shown by a solution of cupric chloride on adding water, etc.

Neutralization and Hydrolysis.—Neutralization is a very familiar type of chemical action. A solution of sodium hydroxide, for instance, turns litmus blue, while one of hydrochloric acid turns it red. We add one to the other in the right proportion and obtain a neutral solution,—one which has no effect on litmus. The chemical change is essentially a reaction between ions, and so in the present chapter we may well study it a little more closely.

The equation may be written $NaOH + HCl \rightarrow NaCl + H_2O$. The first three molecules are all freely ionized, (i) $NaOH$ into Na^+ and OH^-, (ii) HCl into H^+ and Cl^-, and (iii) $NaCl$ into Na^+ and Cl^-. Water, however, is ionized to so slight an extent that in this case we may neglect it. With these points in mind, we may re-write the equation as

$$Na^+ + OH^- + H^+ + Cl^- \rightarrow Na^+ + Cl^- + H_2O. \quad \text{(i)}$$

Similarly, the action of hydrochloric acid on potassium hydroxide might be written

$$K^+ + OH^- + H^+ + Cl^- \rightarrow K^+ + Cl^- + H_2O. \quad \text{(ii)}$$

Notice that in one sense reactions (i) and (ii) are identical, for in both cases the essential change is the formation of *water* by the union of H^+ and OH^- ions. This change is accompanied by the production of heat. If in the two experiments we use equal weights of hydrochloric acid, then equal weights of water will be formed, and we should expect equal amounts of heat to be produced. This is found to be actually the case.

Notice, too, that reactions such as those just discussed are practically *non-reversible;* for as we have just seen, the reaction is essentially $H^+ + OH^- \rightarrow H_2O$, the reverse of which would be $H_2O \rightarrow H^+ + OH^-$, — and water does not ionize to any appreciable extent.

In certain cases, however, the reverse of neutralization *does* take place, such a change being known as **hydrolysis.** Thus, when sodium carbonate is dissolved in water, the solution is alkaline,—a sure sign that OH ions are present in considerable quantity. We conclude that sodium hydroxide has been produced (NaOH, which ionizes freely into $Na^+ + OH^-$). We therefore, write the equation

$$Na_2CO_3 + 2H_2O \rightarrow 2NaOH + H_2CO_3.$$

Let us try to understand why an appreciable left-to-right reaction takes place in this case.

Sodium carbonate ionizes freely ($Na_2CO_3 \rightleftarrows 2Na^+ + CO_3^{--}$), while water ionizes only very slightly ($H_2O \rightleftarrows H^+ + OH^-$). The few hydrogen ions so produced, however, are removed as fast as they are formed, because they combine with CO_3^{--} ions producing carbonic acid, H_2CO_3.

$$2H^+ + CO_3^{--} \rightarrow H_2CO_3.$$

Carbonic acid is a very weak acid (*i.e.* it shows little tendency to ionize, to throw H^+ ions back into solution).

Thus, in the reaction $H_2O \rightleftarrows H^+ + OH^-$, one of the products on the right is continually removed, with the result that the left-to-right reaction goes on,—not to completion certainly, but much further than it otherwise would have gone. Hence, OH^- ions accumulate in the solution

to such an extent as to make it alkaline to litmus. The solution, in fact, contains the ions of sodium hydroxide, Na^+ and OH^-. Notice that this hydrolysis (giving an alkaline solution), takes place because we are dealing with a compound (Na_2CO_3), of a strong base with a weak acid. Conversely, a compound of a weak base with a strong acid, (*e.g.* copper sulphate, $CuSO_4$) gives an acid solution.

Electrochemical Series.—In Fig. 7 we have a plate of copper and one of zinc immersed in dilute sulphuric acid, and connected outside the acid by a wire. The arrangement is known as a *voltaic cell*, and it is found that a current flows through the wire from the copper to the zinc *outside* the liquid, and, therefore, from zinc to copper *inside*. The zinc is said to be "higher than copper" in the electrochemical series. If we repeat the experiment with plates of (a) zinc and iron, (b) iron and copper, we find that iron is higher than copper in the series, but lower than zinc.

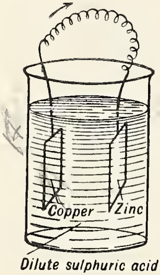

FIG. 7.—Simple voltaic cell.

It is possible, in fact, to arrange the metals one below the other in such an order that, if any two of them were used for making a cell, the direction of the current in the liquid would be from the one higher in the column to the lower. Such an arrangement is called the **electromotive series**, and for some of the principal metals it is given below.

Potassium
Sodium
Calcium
Magnesium
Aluminium
Zinc
Iron
Tin

Now although this list is drawn up in connection with what we may call an *electrical* property of the elements concerned, we soon find that it also expresses some of their *chemical* properties. Thus as we descend the series we find that:—

(1) Any element will displace a lower element from a solution of one of its salts,

Lead	*e.g.* iron displaces copper from a solution
(Hydrogen)	of copper sulphate, magnesium will re-
Copper	place zinc, and so on. An important spe-
Mercury	cial case is that the metals above hydrogen
Silver	will displace this element from acids (an
Gold	acid being regarded as a salt of hydrogen),
	while the metals below it will not.

(2) The metals displace hydrogen from water with increasing difficulty. (This is evidently closely connected with the special case mentioned in (1).) You will find the statement well illustrated in later chapters, where the action of potassium, sodium, calcium, magnesium, and iron on water is discussed, and where it might have been mentioned that copper—below hydrogen in the series—does not decompose water at any temperature.

(3) The oxides are reduced with increasing ease. The oxides of the metals down to zinc cannot be reduced by heating in a stream of hydrogen, and in this respect they differ from those of iron, tin, lead, and copper. Oxides of mercury, silver, and gold are reduced by merely heating, no hydrogen being necessary.

Notice that the metals above zinc have only become known in comparatively recent times. This is because most metals are obtained by reduction of their ores, and the difficulty of the process increases as we ascend the series. The five metals at the top of the list are obtained, not by reduction, but by electrolysis.

(4) The metals oxidize less and less readily. (This perhaps is only the last paragraph from another point of view.) At the one extreme, we have potassium, sodium, and calcium, which it is very difficult to prevent from oxidizing; at the other, we have silver and gold, used in coinage because (among other reasons) they do not oxidize on exposure to the air.

Iron certainly seems to rust more readily than aluminium, but we must remember that the easy rusting of iron is largely due to the fact that iron rust does not form as

closely adhering a coat as aluminium rust. Thus it readily falls off constantly exposing a fresh surface of metal to the action of the air. Aluminium rust sticks tightly on, forming a protective coat over the metal beneath.

There are some other chemical properties of the metals which are closely related to their position in the electromotive series. It is a good plan to know the list by heart.

Questions

1. A storage battery, a lamp, and a copper plate are connected in series. The other wire from the battery is directly connected with a second copper plate. The plates are then immersed successively in (*a*) a solution of cane sugar, (*b*) a very dilute solution of sulphuric acid, (*c*) a considerably stronger solution of the acid. How would you expect the lamp to behave? Give reasons.

2. A dilute solution of ferric chloride ($FeCl_3$) is prepared. How would you expect its freezing point to compare with the value calculated from Raoult's law?

3. 7·45 gm. of potassium chloride is dissolved in 200 c.c. of water. Assuming that the salt is completely ionized, what would be the freezing point of the solution?

4. A man who is not sure which is the positive terminal of his car battery sometimes finds out in this way. He puts the two terminals in a solution of common salt, and finds that from one terminal gas is given off freely, while from the other scarcely any gas appears. The latter, he says, is the positive terminal. Explain.

5. What would you expect to happen if you added concentrated hydrochloric acid to a strong solution of common salt? Account for the result.

6. A concentrated solution of copper bromide (a brown salt) is brown. On diluting it with water it turns green, and on further dilution, blue. On adding a concentrated solution of potassium bromide, it once more becomes green (or even brown). Account for these results. (*Hint.*—Brown includes a large proportion of yellow.)

7. Account for the facts that (i) a solution of ferric chloride is acid to litmus and (ii) a solution of potassium carbonate is alkaline.

8. In carrying out qualitative analysis, we expect the "metal" to give its proper reactions quite independently of the "acid" with which it may be combined, and vice versa. Do you think this has any bearing on the subject of the present chapter?

9. Copper is preferred to iron for making pipes which are frequently exposed to the action of steam (*e.g.* the condenser pipes of locomotives). Why?

10. Why does the blade of your pocket-knife become coated with copper when you dip it in a solution of copper sulphate? Would it injure the blade to leave it in the solution overnight?

11. "Toning" in photography consists essentially in soaking the (silver) print in a bath of gold chloride. The print soon changes in colour, and afterwards, on washing, the wash-water is found to be distinctly milky. Explain what has happened.

12. (*a*) In an ancient Egyptian temple, an image of gold has been found thinly coated over with silver.
(*b*) Homer records that Achilles received a ball of iron for his prowess in the games.
In what way are these statements connected with the electro-chemical series?

CHAPTER V

THE HALOGEN FAMILY

If the eighty or ninety children of a village were all assembled in the village hall and we observed them carefully, we should soon find that in some cases there was a considerable resemblance between one child and another. This resemblance we call a " family likeness ". If we had many opportunities of observing all the children closely —colour of hair and eyes, shape of face, etc.—we might be able to divide them up into families, though no doubt we should make many mistakes.

The chemical elements are rather like these eighty or ninety children, for between some of them there is a remarkable family likeness. One of these families consists of the four elements, fluorine, chlorine, bromine, and iodine. They are called the halogens, or halogen elements. " Halogen " comes from two Greek words meaning " to produce sea-salt ", and this name was given to the family because sea-salt consists mostly of certain compounds of these elements.

We have already studied chlorine in some detail, so here we shall content ourselves with recalling some of its chief properties. It is a gas with a greenish colour and an extremely pungent smell, and it produces very damaging effects if accidentally inhaled. In the presence of moisture it acts as a powerful bleaching agent. It reacts vigorously with most elements forming chlorides, its compound with hydrogen being the familiar hydrogen chloride,—a gas which steams in moist air and dissolves freely in water forming hydrochloric acid.

We shall now deal comparatively with all four elements, dwelling more particularly on those properties which show that they really do belong to the same family.

Physical Properties.—This family likeness is not very evident on a casual inspection of the elements, except that there is a certain similarity as regards smell. If, however, we set out the chief physical properties in tabular form, we are much struck with one point,—there is a fairly steady *gradation.* Thus, fluorine has the lowest boiling point of all (—187°), chlorine boils at a much higher temperature (—34°), bromine higher still at 59°, and iodine highest of all at 184°C. A similar gradation may be noted in the melting points and specific gravities.

Some Physical Properties of the Halogen Elements

Element	Atomic weight	State at ordinary temp.	Specific gravity of liquid	Colour	Melting point	Boiling point	Solubility at 0°C. (gm. per litre)
Fluorine	19	Gas	1·11	Greenish-yellow	—233°C.	—187°C.	(Attacks water)
Chlorine	35·5	Gas	1·55	Green	—101°C.	—34°C.	14·7
Bromine	80	Liquid	3·19	Reddish-brown	—7°C.	59°C.	47·1
Iodine	127	Solid	4·9 (solid)	Black (solid) Purple (vapour)	113°C.	184°C.	0·19

Chemical Properties.—The resemblance between the four elements is seen in a large number of their chemical properties. Of these we shall mention one or two now, and others will be noticed as the chapter proceeds.

(1) They are all univalent. Thus, corresponding to potassium chloride, KCl, we have potassium fluoride, KF, potassium bromide, KBr, and potassium iodide, KI. Such corresponding compounds often show a resemblance in

properties; those just mentioned for instance, all crystallize in cubes.

The most striking resemblances, however, are seen in the compounds with hydrogen, HF, HCl, HBr, and HI. These are all gases which " steam " in moist air, and all are extremely soluble in water, forming acid solutions.

As we pass from fluorine to iodine, these compounds with hydrogen are formed less and less readily. Thus, fluorine and hydrogen combine with explosive violence even in the dark, while to make chlorine and hydrogen combine with similar violence we must expose the mixture to sunlight. Bromine and hydrogen require the application of heat, while iodine and hydrogen require not simply heat, but also the presence of a catalyst; and even then the combination is not complete.

(2) Chlorine, bromine, and iodine are liberated from their compounds by similar methods (see pp. 58-60).

We must now consider the elements fluorine, bromine, and iodine, and a few of their compounds, in a little more detail.

Fluorine.—A compound of calcium known as *fluorspar* which has been known for centuries, has properties in some respects like those of calcium chloride. In 1810 Ampère suggested that it might be a compound of calcium with some unknown element which he called " fluorine ", after the mineral. The story of the attempts made to isolate fluorine is a very interesting one, but we cannot enter into it here, except to say that the work proved to be not only difficult but dangerous, and more than one chemist lost his life in the quest. For over seventy years one failure followed another, but in 1886 the French chemist, Moissan, solved the problem by an electrolytic method.

Fluorine proved to be a pale yellow gas with a very pungent smell. It fumes in moist air, forming hydrofluoric acid and oxygen, mixed with some ozone. It is the most active element known, and combines directly with practically every other element. With hydrogen it combines

explosively even in the dark, and at temperatures as low as —252°C.

As already mentioned, the name fluorine is derived from "fluorspar", (Lat. *fluere* = to flow). Fluorspar was so called because it was (and still is) used as a *flux, i.e.* a substance added to an ore in the process of smelting, in order to form a fusible compound with the earthy matter present. This fusible matter can then be made to flow away, and is thus got rid of. Considerable quantities of fluorspar are mined in Ontario and British Columbia, most of it being used as a flux in metallurgical operations.

Hydrofluoric Acid.—This name is usually given to a solution of hydrogen fluoride (*cf.* hydrochloric acid and hydrogen chloride). It is prepared by distilling powdered fluorspar with sulphuric acid in a lead retort, and allowing the fumes to pass into a lead receiver containing water–

$$CaF_2 + H_2SO_4 \rightarrow CaSO_4 + 2HF.$$

The solution is kept in gutta-percha bottles.

The reason why glass is never used in connection with the preparation or storage of hydrofluoric acid is that the latter attacks it, removing silica from the glass in the form of the gas, silicon fluoride—

$$SiO_2 + 4HF \rightarrow 2H_2O + SiF_4.$$

Hence, hydrofluoric acid is used to *etch* glass. The glass is first covered with wax in which the necessary letters, etc. are scratched with a needle. The acid is then gently "painted" on and left for a few minutes, after which the wax is removed.

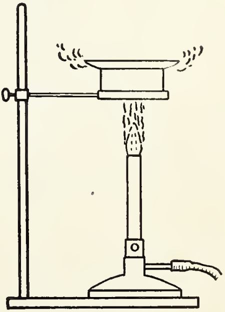

FIG. 8.—Testing for a fluoride.

A watch-glass may easily be etched in the laboratory

by first waxing and scratching it in the way just described, and then making it serve as the cover of a small lead dish which contains a mixture of calcium fluoride and sulphuric acid. On warming the mixture, fumes of hydrogen fluoride are produced and the glass is quickly etched. This reaction is often used as a test for a fluoride.

Hydrofluoric acid has several other uses, all based on the fact that it attacks silica. Thus, it is employed in removing sand from castings.

Bromine.—Bromine is found in nature chiefly as bromides of potassium, magnesium, and calcium. These bromides are present in certain mineral springs, in Germany and Michigan, and in what are known as the Stassfurt deposits (also in Germany),—the residues of ancient seas, the water of which has long since dried up.

To obtain bromine on the large scale, a hot solution of these bromides is treated with chlorine, which causes the bromine to be set free. Thus, with magnesium bromide we should have—

$$MgBr_2 \quad + \quad Cl_2 \quad \rightarrow \quad MgCl_2 \quad + \quad Br_2.$$

The liberated bromine vapour is made to liquefy by passing it into a worm condenser.

In the laboratory, bromine is usually prepared by a method which is easily understood if we recall the usual method of preparing chlorine. The latter consists in heating manganese dioxide with hydrochloric acid, the hydrogen of the acid being converted into water.

$$MnO_2 + 4HCl \rightarrow 2H_2O + MnCl_2 + Cl_2.$$

Instead of hydrochloric acid, however, we may use the substances from which hydrochloric acid is made (a chloride—usually sodium chloride—and sulphuric acid), the complete mixture then being a *chloride,* manganese

dioxide, and sulphuric acid. Correspondingly, to prepare bromine, we use a mixture of a bromide, manganese dioxide, and sulphuric acid. As compounds of metals (potassium and manganese) are present, and also sulphuric acid, we should rather expect potassium and manganese *sulphates* to be formed, and the final equation is actually—

$$2KBr+MmO_2+2H_2SO_4 \rightarrow K_2SO_4+MnSO_4+2H_2O+Br_2.$$

As chlorine is a *gas*, it is collected over (hot) water or by displacement of air. Bromine, however, is a *liquid* with

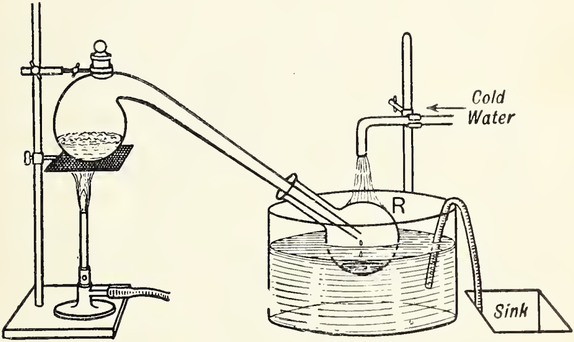

FIG. 9.—Preparation of bromine.

a low boiling point (59°C.). We, therefore, put the materials for its preparation in a *retort,* and heat gently. The bromine vapour readily condenses in the stem of the retort, and drips into the flask.

Iodine may be prepared in a similar way, using potassium iodide instead of bromide. A good deal of the iodine lodges in the neck of the retort, but can be driven forward into the neck of the flask by gently heating.

Preparation of Hydrogen Bromide.—Hydrogen *chloride* may be obtained by the action of sulphuric acid on a

chloride, and so we might expect to obtain hydrogen bromide by the action of sulphuric acid on a bromide—

$$H_2SO_4 \quad + \quad KBr \quad \rightarrow \quad KHSO_4 \quad + \quad HBr.$$

But while the hydrogen chloride is not acted upon by the sulphuric acid, some of the hydrogen bromide produced according to the equation just given is oxidized by the sulphuric acid to bromine, the acid being reduced to sulphur dioxide —

$$H_2O.SO_3 + 2HBr \rightarrow H_2O + SO_2 + H_2O + Br_2,$$

or $$H_2SO_4 + 2HBr \rightarrow 2H_2O + SO_2 + Br_2.$$

Hence the method we are discussing would not be at all suitable. Instead, we make use of the fact that phosphorus tri-bromide, PBr_3, and phosphorus penta-bromide, PBr_5, are decomposed by water according to the equations —

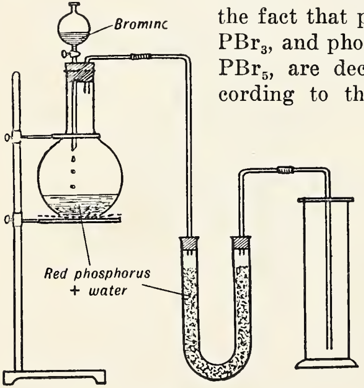

FIG. 10.—Preparation of hydrogen bromide.

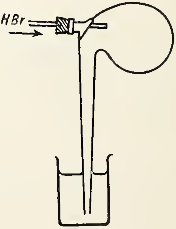

FIG. 10*a*.—Making a solution of hydrogen bromide.

$$PBr_3 \quad + \quad 3H_2O \quad \rightarrow \quad \underset{\textit{Phosphorous acid}}{H_3PO_3} \quad + \quad 3HBr,$$

$$PBr_5 \quad + \quad 4H_2O \quad \rightarrow \quad \underset{\textit{Phosphoric acid}}{H_3PO_4} \quad + \quad 5HBr.$$

Red phosphorus (7 gm.) mixed with water (14 c.c.) is placed in a flask fitted with a dropping funnel containing bromine (14 c.c.). The latter is allowed to fall, drop by drop, into the flask, and there is a rather vigorous action, the heat produced being sufficient to vaporize a considerable amount of the bromine. This bromine vapour is removed by means of the U-tube, which contains broken glass smeared with a mixture of water and red phosphorus. The hydrogen bromide issuing from the U-tube is collected by displacing air upwards in the usual way. If a *solution* of the gas is required, some such device as that shown in the figure must be adopted to prevent "sucking back".

When all the bromine has been added, the flask may be heated to expel some of the dissolved hydrogen bromide. Except for this, there is no need to apply heat.

The phosphorus and bromine react according to the equations—

$$2P + 3Br_2 \rightarrow 2PBr_3 \text{ and } 2P + 5Br_2 \rightarrow 2PBr_5,$$

and the tri- and penta-bromide are then decomposed in accordance with the equations already given.

Hydrogen Iodide.—We have seen that when sulphuric acid acts on a bromide, much of the hydrogen bromide first produced is oxidized (by the sulphuric acid) to bromine, the sulphuric acid being reduced to sulphur dioxide.

In the case of an iodide, this secondary action is much more complete. The hydrogen iodide first produced ($H_2SO_4 + KI \rightarrow KHSO_4 + HI$) is oxidized to iodine, the sulphuric acid being reduced to hydrogen sulphide —

$$H_2SO_4 + 8HI \rightarrow 4H_2O + H_2S + 4I_2.$$

Hence hydrogen iodide cannot be made by the action of sulphuric acid on an iodide. It may be prepared, however, by a method very similar to that just described for hydrogen bromide, only in this case the iodine and phosphorus are placed in the flask, and water is run in from the dropping funnel.

A solution of hydrogen iodide (*i.e.* hydriodic acid) soon goes brown on exposure to the air, owing to liberation of iodine —

$$(2HI + O \rightarrow H_2O + I_2) \qquad 4HI + O_2 \rightarrow 2H_2O + 2I_2.$$

Hydrochloric acid under the same circumstances does *not* produce chlorine. This is another illustration of a fact we have already noted — that hydrogen iodide is much more easily oxidized than hydrogen chloride. As we should expect, hydrogen bromide occupies an intermediate position —bromine is liberated when its solution is exposed to the air, but sunlight is necessary, and even then the oxidation is not so rapid as in the case of hydriodic acid.

Uses.—Bromine itself is not much used outside the chemical laboratory, but potassium bromide is used in medicine and photography. Ethylene bromide, $C_2H_4Br_2$, is now much used as a solvent for the "ethyl lead" often added to motor gasoline.

Iodine.—Minute quantities of iodine compounds are present in sea-water, and so find their way into sea-weed, especially certain deep-sea varieties. The weed, known as *kelp,* is dried and burnt, the iodine (as sodium and potassium iodide) being present in the ashes. These ashes are lixiviated with water and the less soluble compounds are crystallized out, leaving the very soluble sodium and potassium iodides in solution. The solution is now heated with manganese dioxide and sulphuric acid, and iodine distils over. The equations are rather similar to those representing the preparation of bromine from a bromide (p. 59).

The iodine thus obtained is purified by distillation.

Much the greater part of the world's iodine supplies, however, are obtained from Chile saltpetre. The mother liquor which remains after the separation of the sodium nitrate (p. 119) contains a small amount of sodium iodate ($NaIO_3$), and the iodine is obtained from this by somewhat complicated reactions which we shall not discuss here.

Uses.—Tincture of iodine consists of an alcoholic solution of iodine (iodine, ½ oz., potassium iodide, ¼ oz., rectified spirit, 1 pint), and is much used to prevent wounds from becoming septic.

Iodoform, CHI_3, (the iodine compound corresponding to chloroform, $CHCl_3$) is also used as an antiseptic. It is a

yellow crystalline substance with a characteristic smell, and is often made up into an ointment.

Calcium Iodate, $Ca(IO_3)_2$ is coming into use (in countries where food preservation is permitted) as a preservative for milk, butter, fish, etc. It is employed in very minute quantities, but is said to be far superior to boric acid in its power of preventing putrefaction, and to have in many cases a beneficial effect on the health of the consumer.

Iodine is present in the human body (and the bodies of other animals) chiefly in the thyroid gland in the neck. This gland contains not free iodine, but a rather complex substance called thyroxin, in which iodine is present to the extent of 65 per cent. The complaint known as goitre, and some diseases of a more serious character have been traced to the defects of the thyroid gland, and have been treated very successfully by giving doses of iodine, usually in the form of potassium iodide and iodate. It is said that under modern conditions our bodies often fail to obtain sufficient iodine from the food we eat, and so "iodized table salt" has come largely into use. It consists of ordinary salt to which minute quantities of sodium iodide have been added.

During the last few years, various scientists have made experiments on the effect of adding small doses of iodine (usually as potassium iodide) to the food of cattle, poultry, etc., in order to find whether it increases the production of milk and eggs. Some very promising results have been obtained, *e.g.* "Fowls fed on ordinary good meal containing all the necessary mineral elements including iodine, laid, in the month of September 1928, more than twice as many eggs, of greater weight, than similar fowls fed on precisely the same mash with the iodine omitted.[1]" If such results are confirmed by further experiments, there is

[1] *Times Trade and Engineering Supplement,* Chemical Section, 24th November 1928.

no doubt a bright future in store for an element which was once regarded as little more than a chemical curiosity.

Questions

N.B.—See note in italics, p. 20.

1. "The properties of bromine are often a sort of average between those of chlorine and iodine." Illustrate.

2. Explain the derivation of the word *fluorine.*

3. For more than 70 years men tried to extract a new element from fluorspar. Why were they so sure that the element was there?

4. How could you find out whether a given salt was a fluoride? By means of equations explain the reactions that take place in your test.

5. To prepare hydrogen chloride, we heat a chloride with concentrated sulphuric acid. Why do we not prepare hydrogen bromide by treating a bromide with this acid?
   How is hydrogen bromide prepared?

6. The Chilean output of iodine is about 1000 tons per annum. What weight of sodium iodate ($NaIO_3$) would be required to produce this?

7. 220 c.c. of chlorine, measured at 15°C. and 75 cm. pressure, is passed into an aqueous solution of potassium iodide. What weight of iodine would be liberated?

8. 2 gm. of a mixture of potassium bromide and potassium chlorate are weighed out and dissolved in water. Excess of silver nitrate solution is added, and the precipitate of silver bromide is filtered off. After being washed out and dried this is found to weigh 1·88 gm. Find the percentage of potassium bromide in the original mixture.

9. Assuming that by treatment with suitable quantities of water and red phosphorus, 6 gm. of bromine are completely converted into hydrogen bromide, what volume of the latter gas would be obtained if measured at 12°C. and 74·6 cm. pressure?

CHAPTER VI

THE PERIODIC LAW

We have just had a good example of a *family* of elements, and we saw that many of the properties of bromine are about half-way between those of chlorine and iodine. It is worth noticing that its atomic weight is also about half-way, for $Cl=35\cdot5$ and $I=126\cdot9$. The average of these num bers is $81\cdot2$ and the atomic weight of bromine is 80. If this case stood alone we might think we had simply met with a rather odd coincidence, but there are other examples. Thus, lithium (atomic weight 7), sodium (23), and potassium (39) are three members of a family in which the properties of sodium are about mid-way between those of lithium and potassium,—and its atomic weight (23) is the average of 7 and 39. Here are a few other cases:—

Phosphorus	Arsenic	Antimony	
31	75	120	$\frac{31 + 120}{2} = 75\cdot5$
Calcium	Strontium	Barium	
40	88	137	$\frac{137 + 40}{2} = 88\cdot5$
Sulphur	Selenium	Tellurium	
32	79	127	$\frac{32 + 127}{2} = 79\cdot5$

In a number of cases, then, it seems that when the *properties* of an element are about half-way between those of two others, its *atomic weight* is also about half-way between; and this may well make us wonder whether there is not some close connection between the atomic weight of an element and its properties.

A great Russian chemist named Mendeléeff was greatly interested in this question, and in 1869 he wrote down all the elements then known in the order of their atomic weights, using a special arrangement of rows and columns which we shall describe presently. A modern form of the list is given on the two following pages, and elements discovered since 1869 have been included. They are indicated by italics.

He noticed that after seven elements had been written down beginning with lithium, the properties of the *eighth* element, sodium, were to some extent similar to those of the first, lithium[1]. Similarly, the ninth element (magnesium) resembled the second (beryllium) and so on,—a familiar case is that the fourteenth element chlorine is to some extent a repetition of the seventh (fluorine). It is very like playing up the scale on the piano. After the first seven notes have been played we come to another seven which very much resemble the first set,—the second set is in fact the " octave " of the first. To be quite accurate, Mendeléeff was not the discoverer of this " Law of Octaves ", for it had been pointed out five years earlier by a young English chemist named Newlands. We shall soon see, however, that Mendeléeff's discoveries went far beyond those of Newlands.

After completing the second " octave " with chlorine, Mendeléeff found that a third octave seemed to begin quite properly with potassium (which resembles sodium), but on the whole this third series was by no means a repetition of the first two. Manganese, for instance, bears little resemblance to chlorine. Further, counting from potassium he had to write not seven elements, but seventeen, before he came to one (rubidium) which clearly belonged to the potassium family.

Let us notice carefully the arrangement of this " first long period " as the seventeen elements are sometimes

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[1] In the discussion which follows, the " Group O " elements are ignored, as they were not known in 1869.

called. (It is Period 4 in our form of the table.) Mendeléeff divided it into

(*a*) an " even series " of seven elements (series 4 in our table),

(*b*) three " transitional " elements,

(*c*) an " odd " series of seven (series 5).

The " sevens " are placed in the same columns as the first two octaves, but " even series " elements are always placed to the left forming a column known as " sub-group A" or "family A", and "odd series" elements to the right, forming " family B ".

The same procedure was adopted with the " second long period " (Period 5 in our table) of seventeen elements. The remaining elements appeared to form fragments of three other very incomplete long periods, but are now believed to be portions of a very long period (Period 6) of 32 elements and a final short period of 7.

It will be seen that the elements of the first two " short periods " (*i.e.* what we have hitherto called octaves) are placed in family A or B according to which element in the long series they happen to resemble. The first two elements in each short period belong to family A and all the others to family B.

If we now consider the table as a whole, a number of interesting points soon become evident.

(1) The halogen elements occur in the same column (Group VIII, family B), and so do calcium, strontium, and barium, which are all precipitated by ammonium carbonate in the course of analysis. In other cases, too, elements with similar chemical properties are found in the same column.

(2) As we advance from Group I to Group VII, there is a steady change in valency. Group I elements are usually univalent, Group II elements, divalent, and so on, until we come to the quadrivalent elements of the fourth group (*e.g.* carbon forms CH_4 and CO_2). After this the

Periodic

PERIOD	SERIES	Group O A	Group O B	Group I A	Group I B	Group II A	Group II B	Group III A	Group III B	Group IV A	Group IV B
1	1			H 1·0 **1**							
2	2		*He* 4·0 **2**	Li 6·9 **3**		Be 9·1 **4**			B 11·0 **5**		C 12·1 **6**
3	3		*Ne* 20·2 **10**	Na 23·0 **11**			Mg 24·3 **12**		Al 27·1 **13**		Si 28·3 **14**
4	4		*A* 39·9 **18**	K 39·1 **19**		Ca 40·1 **20**		*Sc* 44·1 **21**		Ti 48·1 **22**	
	5				Cu 63·6 **29**		Zn 65·4 **30**		Ga 69·9 **31**		Ge 72·5 **32**
5	6		*Kr* 82·9 **36**	Rb 85·4 **37**		Sr 87·6 **38**		Yt 89·0 **39**		Zr 90·6 **40**	
	7				Ag 107·9 **47**		Cd 112·4 **48**		In 114·8 **49**		Sn 119·0 **50**
6	8		*Xe* 130·2 **54**	Cs 132·8 **55**		Ba 137·4 **56**		15 *Rare Earths* **57 -71**		*Hf* 178·6 **72**	
	9				Au 197·2 **79**		Hg 200·6 **80**		Tl 204·0 **81**		Pb 207·1 **82**
7	10		*Rn* 222·4 **86**	—* **87**		*Ra* 226·4 **88**		*Ac* **89**		Th 232·4 **90**	
Oxygen compounds		—		R_2O		RO		R_2O_3		RO_2	
Hydrogen compounds		—								RH_4	

*See footnote on next page.

Table

Group V A B	Group VI A B	Group VII A B	Group VIII		
N 14·0 **7**	O 16·0 **8**	F 19·0 **9**			
P 31·0 **15**	S 32·1 **16**	Cl 35·5 **17**			
V 51·0 **23** As 75·0 **33**	Cr 52·0 **24** Se 79·2 **34**	Mn 54·9 **25** Br 79·9 **35**	Fe 55·8 **26**	Co 59·0 **27**	Ni 58·7 **28**
Nb 93·5 **41** Sb 120·2 **51**	Mo 96·0 **42** Te 127·5 **52**	*Ma* **43** I 126·9 **53**	Ru 101·7 **44**	Rh 102·9 **45**	Pd 106·7 **46**
Ta 181·0 **73** Bi 208·0 **83**	W 184·0 **74** *Po* **84**	*Re* **75** —* **85**	Os 109·9 **76**	Ir 193·1 **77**	Pt 195·2 **78**
Pa **91**	U 238·4 **92**				
R_2O_5 RH_3	RO_3 RH_2	R_2O_7 RH	RO_4		

*Indications of the presence of elements of atomic numbers 85 (alabamine) and 87 (virginium) have been obtained, but the evidence is at present rather inconclusive.

valency with reference to hydrogen falls regularly (*cf.* NH_3, OH_2, FH, in the first short period), though the *maximum* valency with reference to oxygen appears still to rise.

(3) The elements on the left of the table, beginning with Group I, are strongly electro-positive. As we move to the right this property becomes less marked and gradually gives place to electro-negativeness, the latter property reaching a maximum on the right of the table (Group VII). A good example is seen in the second short period, where sodium is more electro-positive than magnesium and magnesium than aluminium (*cf.* table on p. 50). After aluminium we have a feebly electro-negative element, silicon, and then electro-negative properties increase until they reach a maximum in chlorine.

It will be clear from what has been said that change in atomic weight is accompanied by a roughly parallel change in properties, and we shall find many other examples of this as we continue our study of elements and compounds. Mendeléeff summed up the situation in his **Periodic Law**, which may be briefly stated thus: *When the elements are arranged in the order of their atomic weights, there is a periodic recurrence of properties both of the elements themselves and of their corresponding compounds.*

Correction of Atomic Weights.—When Mendeléeff first published his table there were a number of cases in which the accepted atomic weight would not "fit". Indium, for instance, was believed to have an atomic weight of 76, but this would bring it between arsenic (75) and selenium (79), where there was no vacant space. Several chemists argued that the Periodic System must be at fault. "No," said Mendeléeff boldly, "it is the atomic weight that is at fault!" Naturally, special attention began to be paid to the atomic weight of indium.

Its equivalent was certainly 38, and its valency had been thought to be 2, giving an atomic weight of $38 \times 2 = 76$. The element was found, however, to have a specific heat

of ·057, and therefore its *approximate* atomic weight should be $6 \cdot 3 \div \cdot 057 = 111$. Now, its exact atomic weight must be a multiple of 38, *i.e.* it must be one of the numbers 38, 76, 114, 152 . . . etc. As the approximate value is 111, we naturally select the value 114, the valency then being 3. Now in the table there *was* a vacant space between cadmium = 112, and tin = 119, so with the new value, 114, indium fitted in very well. In several other cases the Periodic System was the means of correcting faulty atomic weights.

Prediction of New Elements.—The table as it appeared in 1869 contained a number of blanks which have since been filled in. There was a blank, for instance, in the space now occupied by gallium in Period 5. In 1871 Mendeléeff not only predicted the discovery of the element, but by considering the properties of the elements above and below (aluminium and indium) and to the left (zinc), —the space to the right now occupied by germanium was at that time blank,—he was able to make a very close forecast of the properties of an element that nobody had ever seen! "Eka-aluminium" he provisionally called this new element, and it is interesting to compare the properties he predicted for it, with those of "gallium" which was discovered and named four years later, *i.e.* in 1875.

Eka-aluminium	*Gallium*
Atomic weight will be about 69.	Atomic weight, 69·9.
Its melting point will be low.	Melting point, 30·15°C.
Specific gravity will be about 5·9.	Specific gravity, 5·93.
Will not be affected by air.	Only slightly oxidized even at red heat.
At a red heat it will decompose water.	Decomposes water at high temperatures.

Eka-aluminium	*Gallium*
Will form an oxide El_2O_3, a chloride El_2Cl_6 and a sulphate $El_2(SO_4)_3$.	Gallium oxide is Ga_2O_3, the chloride is Ga_2Cl_6 and the sulphate $Ga_2(SO_4)_3$.
The metal is likely to be more volatile than aluminium, and will probably be discovered by means of the spectroscope.	Was discovered by the spectroscope in 1875.

In a similar way Mendeléeff made a very accurate forecast of the properties of scandium (discovered in 1879) and of germanium (1886).

A New Group of Elements.—In 1894 Ramsay discovered in the atmosphere a hitherto unrecognized gas which he called *argon.* This discovery caused him to make a very careful examination of the atmosphere to see if there were any other gases awaiting discovery. Within the next two years he found four, *viz.* helium, neon, krypton, and xenon! These are present only in extremely small amounts; xenon, for instance, to the extent of only one part per 20 million parts of air.

There was naturally much curiosity as to the place of these new gases in the Periodic Table. Their atomic weights were determined, and it was found that they came to the left of Group I, forming Group O, in fact. We have already seen that the valency of the elements in Group III is 3, in Group II is 2, and in Group I is 1. Very fittingly, the elements in the new group have a valency of 0, for they do not form any compounds with other elements.

Radon, the element of highest atomic weight in Group O, was found not in the atmosphere but in connection with radium.

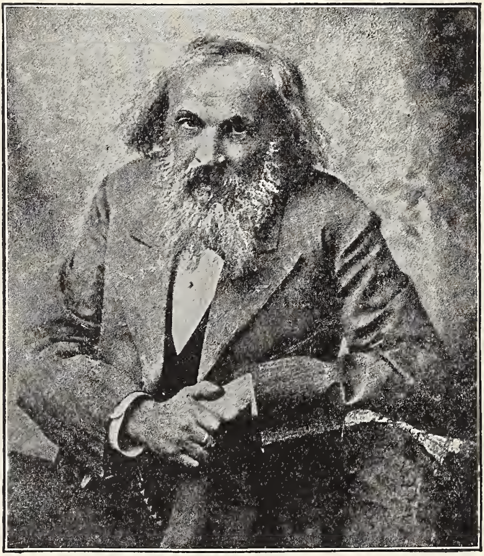
Defects in the Periodic System.—We have already seen how greatly the science of chemistry has been advanced by the Periodic System. Faulty atomic weights have been corrected, and information has been gained about the

existence and properties of new elements. Less striking but, perhaps, of more solid importance is the fact that the periodic system gives us a scientific *classification* of the elements. For instance, it divides them up according to valency, and it divides off metals from non-metals and shows how the one kind of element shades off into the other.

Yet the system is not without its defects. It separates certain elements which have strong points of similarity (*e.g.* copper and mercury; barium and lead) and it brings together elements which have very little in common (*e.g.* manganese and chlorine). Again, there are several cases in which elements can only be placed in their proper group according to properties by disturbing the order of the atomic weights. A famous example is that of iodine and tellurium. According to properties, tellurium (which resembles sulphur and selenium) should certainly come *before* iodine (which obviously belongs to the chlorine family). Yet its atomic weight is actually a little *higher* (127·5 as compared with 126·9). Another case is that of argon (Group O, atomic weight, 40) and potassium (Group I, but atomic weight, only 39). These cases of reversed atomic weight perplexed scientists for something like forty years, and then it was found that the most essential thing about an element is not its atomic weight, but its *atomic number*. The atomic numbers are given in black type in our table, just below the symbols of the respective elements; of course, they did not appear at all in Mendeléeff's original table, for at that time nothing was known about them.

A proper understanding of the meaning of "atomic number" takes us into the question of atomic structure, and we shall postpone this to Chapter XXVIII; but we may say now that such irregularities as iodine-tellurium and potassium-argon disappear when the elements are arranged not according to atomic weight but atomic number.

We ought not to leave the subject of the Periodic System without knowing just a little about its discoverer. Dmitri Ivanovitch Mendeléeff was born in 1834 at Tobolsk in Siberia, the youngest of a family of fourteen. He was



DMITRI IVANOVITCH MENDELEJEFF

still quite a small boy when, from conversations with a political exile named Basargin, he acquired a love of science. The chance of receiving any definite instruction, however, seemed very remote, and must have seemed more remote than ever when his father died while the boy was still only thirteen years old.

But Dmitri's mother was a very remarkable woman who was determined that her son should have his chance. In

those days there was no trans-Siberian railway, but she took him with her on the tedious 1200-mile journey to Moscow, " spending thus her last resources and strength," as her son wrote years afterwards. At Moscow she failed to get any assistance, but after several other rebuffs she succeeded in getting him admitted to a sort of University College at St. Petersburg. At last Dmitri had obtained his opportunity, and he made such use of it that long before his death in 1907 he had taken a high place among the world's great scientists.

Questions

1. On p. 65, it is shown that in several cases, taking three consecutive members of a family of elements, the atomic weight of the middle one is approximately the average of the atomic weights of the two others. Examine the table on pp. 68, 69 and find two other examples for yourself. Also find two examples in which the relationship does not hold good.

2. In 1864 Newlands discovered the " Law of Octaves ". Would this term apply equally well today?

3. The position of hydrogen in the periodic table has been the subject of much controversy. Give any reasons you can (*a*) in favour of the position assigned to it on p. 68, and (*b*) against that position.

4. In the years 1894-5 Ramsay discovered five new elements. From an examination of the table on pp. 68, 69, do you think such an achievement will ever be repeated? Give your reason.

5. In what ways has the Periodic system advanced the science of chemistry?

6. On page 73, it is pointed out that in order to fit tellurium and iodine into the Periodic Table, we have to alter the order of their atomic weights, and similarly with regard to argon and potassium. The table contains one other such example. Find it.

7. Write an account of the life of Mendeléeff, obtaining the facts from anywhere you can.

CHAPTER VII

THE NITROGEN-PHOSPHORUS FAMILY

IF you refer to the table on pp. 68, 69, you will find that Group V, family B consists of the elements nitrogen, phosphorus, arsenic, antimony, and bismuth. Let us first of all consider the family as a whole.

In the order of increasing atomic weight ($N = 14$, $P = 31$, $As = 75$, $Sb = 120$, $Bi = 208$), we notice that the physical properties change from those of a non-metal to those of a well-defined metal. Thus, at very low temperatures nitrogen solidifies to a white solid with no suggestion of metallic lustre. Phosphorus in one of its forms is a dull red powder and in another a waxy-looking solid. With arsenic we first find the lustre characteristic of a metal; in the case of antimony and bismuth the metallic appearance is very clearly marked. Another point worth noting is the steady increase in density, because, broadly speaking, low density is characteristic of a non-metal and high density of a metal. The relative densities are:—nitrogen (solid) 1·026, phosphorus (red) 2·20, arsenic 4·71, antimony 6·62, and bismuth 9·78.

The same transition from non-metal to metal is seen in the chemical properties. The oxide of a non-metal is usually acid-forming; that of a metal is basic (p.   ). Now, nitrogen pentoxide, N_2O_5, with water forms nitric acid ($N_2O_5 + H_2O \rightarrow 2HNO_3$); bismuth trioxide is basic, for it neutralizes acids giving salts such as bismuth nitrate, $Bi(NO_3)_3$. As we pass from nitrogen to bismuth the oxides become less acidic and more basic in character, and in the case of arsenic the acidic and basic properties are about evenly balanced. Arsenic, in fact, is known as a *metalloid,*

i.e. an element on the border line between metal and non-metal.

Then, non-metals usually form with hydrogen stable compounds known as *hydrides;* metals do not, and in this respect, also, we have a steady transition from the one to the other. Thus, nitrogen forms the well-known hydride ammonia, NH_3. At the other end of the series, bismuth forms no hydride at all, or at most a very unstable one (there is some doubt on this point). Between these extremes the hydrides, PH_3, AsH_3, SbH_3, show decreasing stability as we approach bismuth.

Having thus glanced at the family as a whole, we shall now consider the properties of some of its individual members and of certain of their compounds. Nitrogen will have already been dealt with, so we shall begin with phosphorus.

Phosphorus

Occurrence and Extraction.—Phosphorus oxidizes so readily that it could hardly occur in nature in the free condition. The most important compound that occurs naturally is calcium phosphate, $Ca_3(PO_4)_2$. This is found in many parts of the world, *e.g.* as "phosphate rock" in South Carolina and Florida. There are deposits in British Columbia which are being investigated but have not yet been worked on a large scale.

Calcium phosphate also occurs in bones to the extent of about 58 per cent.

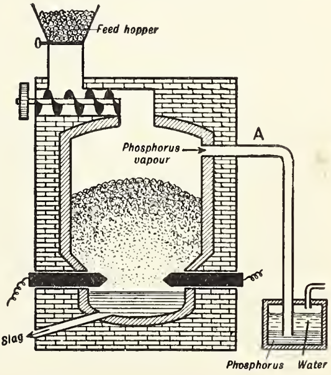


Fig. 11.—Manufacture of Phosphorus by the Electric Furnace.

At the present time phosphorus is extracted from phosphate rock or from bone ash by means of the electric furnace. Conveyed by a sort of screw, a mixture of calcium phosphate, sand, and coke is fed into the furnace, which is raised to a very high temperature by an electric arc struck between the carbon electrodes. Phosphorus vapour mixed with carbon monoxide passes through the pipe A. This bends down at right angles and dips under water, at the bottom of which the phosphorus collects. Molten calcium silicate collects at the bottom of the furnace and is run off from time to time through the slag-hole. Let us now try to understand the chemical changes that take place.

We may regard calcium phosphate, $Ca_3(PO_4)_2$, as being $3CaO + P_2O_5$ (basic oxide + acidic oxide). Sand contains silica, SiO_2, another acidic oxide. We may think of the SiO_2 as competing with the P_2O_5 for possession of the CaO, and competing successfully, because at the high temperature of the furnace phosphorus pentoxide is volatilized, while silica is not. Thus we have—

$$(3CaO).P_2O_5 + 3SiO_2 \rightarrow 3(CaO.SiO_2) + P_2O_5,$$

$$\text{or} \quad Ca_3(PO_4)_2 + 3SiO_2 \rightarrow 3CaSiO_3 + P_2O_5 \quad (a).$$

The pentoxide is now reduced by the heated coke—

$$P_2O_5 + 5C \rightarrow 5CO + 2P \quad (b).$$

Adding (*a*) and (*b*), and cancelling P_2O_5, which comes on both sides, we obtain the complete equation—

$$Ca_3(PO_4)_2 + 3SiO_2 + 5C \rightarrow 3CaSiO_3 + 5CO + 2P \quad (c).$$

The manufacture of phosphorus is carried out chiefly at Niagara Falls, where cheap electric power is obtainable. The world output is about 5000 tons per year, most of it being used in the manufacture of matches, while some is employed in making *phosphor bronze,* a valuable alloy.

Two Forms of Phosphorus.—The phosphorus obtained in the way just described has to be purified. It is then found to be a pale yellow solid (colourless if very pure), with a crystalline appearance when broken across. When

heated to a special temperature—about 240°C.—in an atmosphere of nitrogen or carbon dioxide, it is changed into an allotropic form known as red phosphorus. As it does so, much heat is evolved. From this it is evident that red phosphorus possesses less energy than the yellow form, and we shall therefore expect to find that it is less chemically active.

Properties.—We shall deal first with yellow phosphorus. Phosphorus means " light bearer ", and it was so called because the men who first examined it were chiefly impressed by the fact that it glowed in the dark. Readers of *The Cloister and the Hearth* will remember that this property is the basis of a very exciting " robber " scene, but unfortunately the story deals with late fifteenth century life, and phosphorus was not discovered till about 1670, by the physician Brand of Hamburg.

The glowing is the result of slow oxidation. This process is sufficient in the course of a few hours to remove the oxygen from the air contained in a glass vessel.

With a very slight rise of temperature phosphorus takes fire in air, giving off copious white fumes of phosphorus pentoxide ($P_4 + 5O_2 \rightarrow 2P_2O_5$). Thus, phosphorus is always kept under water, and must never (except when under water) be handled with the fingers. Phosphorus burns are very painful and take a long time to heal.

It is very soluble in carbon disulphide. If the solution is poured on a filter paper, the phosphorus takes fire as soon as the disulphide has evaporated.

This is because the phosphorus left behind is in a very finely divided condition, and so the total *area* at which phosphorus and oxygen are in contact is very large.

Yellow phosphorus is extremely poisonous, and is a common ingredient in the poisons used for rats and other vermin.

In contrast with the properties just mentioned, red phosphorus does not glow in the dark, and does not readily take fire in air (it has to be heated to about 240°). Thus it is

quite safe to handle. When it *does* burn, however, the action is the same as already described. It is insoluble in carbon disulphide, and is non-poisonous. (Remember, however, that an ordinary sample of red phosphorus would contain about 0·5 per cent. of the highly-poisonous yellow variety.)

Red phosphorus has a higher specific gravity (2·20) than yellow (1·83). It consists of crystals so small that it was long thought to be amorphous; the crystalline structure of yellow phosphorus is well marked.

We have seen how yellow phosphorus may be converted into red. The opposite change is easily brought about by heating red phosphorus in an atmosphere of carbon dioxide, as indicated in Fig. 12. Drops of molten yellow phosphorus condense on the upper part of the tube.

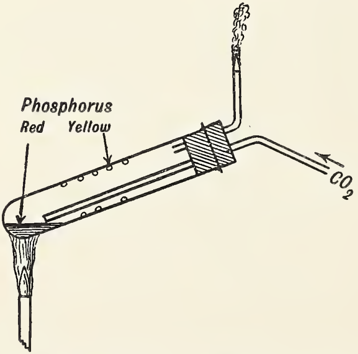


FIG. 12.—Making yellow phosphorus from red.

Oxides. Phosphoric Acid. Phosphates.—Phosphorus forms at least three oxides having the formulae P_2O_3, P_2O_4, and P_2O_5, respectively (*cf.* oxides of nitrogen). Of these, the pentoxide, P_2O_5, is the most important.

We can easily prepare a small specimen by placing a fragment of phosphorus in a crucible which rests on a tile,

and then setting fire to it by means of a hot wire. A bell-jar is placed over the top, and the dense fumes[1] of pentoxide settle as a white powder on the inside of the jar. If exposed to the air it soon becomes damp owing to absorption of moisture, which turns it into *metaphosphoric acid* (HPO_3)—

$$P_2O_5 + H_2O \rightarrow 2HPO_3.$$

Phosphorus pentoxide, in fact, is the most powerful drying agent we possess.

When boiled with water, metaphosphoric acid is changed into orthophosphoric acid, H_3PO_4—

$$HPO_3 + H_2O \rightarrow H_3PO_4.$$

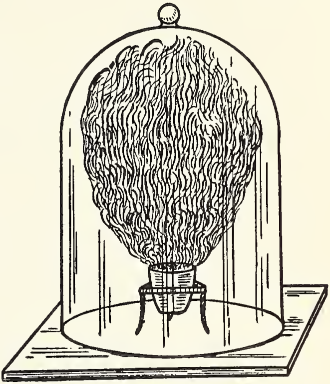


FIG. 13.—Making phosphorus pentoxide.

A better way of making orthophosphoric acid, however, is to oxidize red phosphorus by means of nitric acid, diluted with an equal volume of water to moderate the violence of the action.

$$5HNO_3 + P \rightarrow H_2O + 5NO_2 + H_3PO_4.$$

To obtain the equation mentioned above we think of nitric acid, HNO_3, as $H_2O . N_2O_5$, and of orthophosphoric acid, H_3PO_4, as $3H_2O . P_2O_5$. We must also remember that the nitric acid is reduced to nitrogen peroxide, NO_2.

Now in becoming NO_2 (or rather $2NO_2$), $H_2O . N_2O_5$ loses *one* atom of oxygen; but to become P_2O_5 two atoms of phosphorus must gain *five* atoms. Thus 2P must react with *five* times $H_2O . N_2O_5$. This gives us—

$$5(H_2O . N_2O_5) + 2P \rightarrow 5H_2O + P_2O_5 + 10NO_2,$$
$$\rightarrow (3H_2O + P_2O_5) + 2H_2O + 10NO_2,$$

i.e. $$10HNO_3 + 2P \rightarrow 2H_3PO_4 + 2H_2O + 10NO_2.$$

Dividing through by 2 we obtain the equation already given.

[1] During the Great War phosphorus was sometimes used for producing a smoke-screen.

We have already seen that the calcium salt of orthophosphoric acid, $Ca_3(Po_4)_2$, occurs in nature. A solution of one of the *sodium* salts, Na_2HPO_4 (disodium hydrogen phosphate), is much used in "testing for magnesium". The suspected magnesium salt is dissolved in water, and ammonium chloride and ammonium hydroxide are added (the ammonium chloride serves to prevent the precipitation of magnesium as hydroxide). If sodium phosphate is now added, a white precipitate of magnesium ammonium phosphate is obtained—

$$MgSO_4 + Na_2HPO_4 + NH_4OH \rightarrow MgNH_4PO_4 + Na_2SO_4 + H_2O.$$

Just as plants need combined *nitrogen* as food (p. 136), they also need combined *phosphorus*. The subject of phosphorus as a fertilizer will be taken up in Chapter XII.

Phosphine.—Phosphorus forms several compounds with hydrogen, one of them being the gas phosphine, PH_3. We must notice this briefly because it is evidently the compound of phosphorus which corresponds to ammonia, NH_3. Further, just as ammonia will give rise to ammonium chloride ($NH_3 + HCl \rightarrow NH_4Cl$), so, at low temperatures, phosphine will give rise to phosphonium chloride ($PH_3 + HCl \rightarrow PH_4Cl$).

As phosphine can give rise to salts, it is evidently to some extent basic. Unlike ammonia, however, phosphine is only slightly soluble in water, and its solution is not alkaline to litmus. Evidently then, it is a much weaker base than ammonia.

Matches.—Matches in something like their modern form were invented about the year 1832. The head consisted of yellow phosphorus, mixed with an oxidizing agent such as potassium chlorate, $KClO_3$; red lead, Pb_3O_4; manganese dioxide, MnO_2; etc., and a little gum to hold it together. On rubbing the match against sandpaper, the friction raised the temperature sufficiently to start a chemical action. This consisted of rapid oxidation of the phosphorus, first by the oxygen obtained from the potassium chlorate, etc., and then by the oxygen of the air. The oxidation was so vigorous as to be accompanied by flame.

As already mentioned, however, yellow phosphorus is a deadly poison, and since 1912 the manufacture of matches containing yellow phosphorus has been prohibited, practically throughout the world. The strike-anywhere match of today contains not phosphorus, but a *sulphide* of phosphorus, P_4S_3, mixed with an oxidizing agent as before. Since the phosphorus is oxidized to pentoxide and the sulphur to dioxide, we can easily calculate that 16 atoms of oxygen will be required (10 for the phosphorus and 6 for the sulphur), so we may write the equation—

$$P_4S_3 + 8O_2 \rightarrow 2P_2O_5 + 3SO_2.$$

The safety match, intended to strike only on a prepared surface, was invented as long ago as 1844. The head of the match contains various oxidizing agents (*e.g.* potassium chlorate and red lead) mixed with antimony sulphide, Sb_2S_3. The essential constituent of the prepared surface is red phosphorus. When the match head rubs against this, a little of the phosphorus is at once oxidized by the oxygen contained in the potassium chlorate,[1] red lead, etc. The heat thus produced is sufficient to start the main chemical action, which takes place in the match itself between the antimony sulphide and the various oxidizing agents.

$$[Sb_2S_3 + 9O \rightarrow Sb_2O_3 + 3SO_2]$$
$$2Sb_2S_3 + 9O_2 \rightarrow 2Sb_2O_3 + 6SO_2.$$

A good match should soon cease to glow when blown out (otherwise there is some risk of fire being caused). To secure this, the splints, before receiving their heads, are boiled for two hours in a solution of borax, a substance containing much water of crystallization. You can no doubt think out for yourself how the presence of such a substance would help to prevent glowing.

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[1] Many a burnt pocket has resulted from this reaction. A man has bought "throat tablets" consisting of potassium chlorate, and one or two of these have escaped from the packet and rubbed against the surface of his match-box. With one of these tablets and a (safety) match-box it is easy to light a bunsen burner.

Arsenic

Occurrence and Extraction.—Arsenic is sometimes found free in nature, but its commonest ore is *arsenopyrite* or *mispickel*, FeAsS, which is widely distributed in many parts of the world, including Canada. Most of the arsenic produced in this country, however, is obtained as a by-product in the smelting of silver-cobalt ores, especially at Deloro. When such ores are being roasted, the arsenic is oxidized to arsenious oxide, which volatilizes and may be collected in suitable flues. The crude product is purified by re-sublimation, and the pure oxide thus obtained is the source of all the arsenic compounds used in industry.

The element is obtained by mixing the oxide with charcoal and heating in a clay crucible. Over this is an inverted iron cone, and a sublimate of arsenic collects in it—

$$As_4O_6 \quad + \quad 6C \quad \rightarrow \quad 6CO \quad + \quad As_4.$$

Properties.—Like phosphorus, arsenic occurs in several allotropic forms, the usual variety being known as " grey arsenic ". This forms steel-grey, metallic-looking crystals, which conduct heat and electricity fairly well. At 450° it sublimes rapidly without first melting, forming a colourless vapour. In oxygen it burns with a brilliant flame, forming arsenious oxide ($As_4 + 3O_2 \rightarrow As_4O_6$).

Another allotropic form is known as "yellow arsenic ". This consists of light yellow crystals which rapidly oxidize in the air at room temperature, glowing faintly and giving an odour of garlic,—behaviour which reminds us strongly of phosphorus. On exposure to light the unstable yellow arsenic is quickly transformed into the stable "grey arsenic " (*cf.* action of light on white phosphorus, which is slowly turned into the red variety).

Vapour density determinations show that at a temperature of 860°C. the molecule of arsenic consists of four atoms, another point of similarity to phosphorus. The vapours of metals are usually monatomic, so in this respect arsenic behaves rather like a non-metal.

Compounds of arsenic have a number of uses as mentioned in the next paragraph. The *element* arsenic is used chiefly in connection with the manufacture of lead shot It is found that by adding a small quantity (one per cent, or less) to lead, the latter when melted is more fluid, and thus when run into water through a sieve, it more readily assumes the spherical shape. Further, the shot after solidifying is considerably harder than pure lead would be.

Arsenious Oxide, As_4O_6, commonly known as *white arsenic* or simply *arsenic,* is obtained as already described when smelting various ores, and notably cobalt-silver ores.

As usually met with it is a white powder only slightly soluble in water. It dissolves in hydrochloric acid, forming arsenious chloride, and in caustic soda forming sodium arsenite.

$$As_4O_6 + 12HCl \rightarrow 4AsCl_3 + 6H_2O.$$

$$As_4O_6 + 12NaOH \rightarrow 4Na_3AsO_3 + 6H_2O.$$

The first reaction would incline us to think that arsenious oxide is basic, while the second suggests that it is acidic. The fact is that it is **amphoteric**, an adjective applied to *an oxide which is sometimes acidic and sometimes basic* (Gr. *amphoteros* = both). The existence of such an oxide is another good reason for regarding arsenic as being on the borderline between metal and non-metal (pp. 76-7).

White arsenic is often employed in making rat-poisons and (usually dissolved in caustic soda to form sodium arsenite) as a constituent of sheep dips. It also acts as a preservative for wood, its poisonous qualities preventing the development of certain low forms of life associated with decay. Large quantities are used in the preparation of lead arsenate (*q.v.*), which is employed as an insecticide in agriculture and horticulture, and as a means of dealing with such pests as the locust and the bool-weevil. Arsenious oxide also enters into the preparation of certain pigments and enamels, and is used as a decolorizer in the plate-glass industry.

Government analysts keep a sharp look-out for traces of white arsenic in certain foods. It may happen that at some stage in their preparation, sulphuric acid is used, and the sulphur ores used in the manufacture of the acid are frequently associated with arsenic. Thus, it has occasionally happened that by this roundabout process, food has become contaminated with arsenic. Extremely delicate tests are available, one of which is described in the next paragraph.

Arsine.—Corresponding to ammonia, NH_3, and phosphine, PH_3, we have arsine, AsH_3. Remembering that ammonia is definitely basic and phosphine very feebly so, we should expect to find that arsine is not basic at all, and this is the case. It forms no compound, for instance, corresponding to NH_4Cl and PH_4Cl. Like phosphine, it is insoluble in water.

Arsine is produced when any compound of arsenic is reduced with nascent hydrogen, and its formation gives us a delicate test for the presence of arsenic. A hydrogen generator is set up and, taking the usual precautions, the gas is lit at the exit tube. On pouring a little solution of an arsenic compound down the thistle-funnel, the flame at once assumes a curious greenish-grey colour, and white fumes of the oxide As_4O_6 are given off. On holding a porcelain dish against the flame a black deposit of arsenic is produced upon it. This deposit readily dissolves in a solution of bleaching powder (Antimony compounds give a similar reaction, but in this case the black deposit—of antimony—is insoluble in the bleaching powder solution).

FIG. 14.—Testing for arsenic.

In a modified form the test just described is used to detect the presence of extremely small quantities of arsenic,

e.g. in poisoning cases such as one sometimes reads about in the newspapers. In this case the hydrogen, carefully dried and purified, is made to pass through a glass tube ACB drawn out as shown in the figure. On heating the tube at C, there should be no darkening of the portion CB.

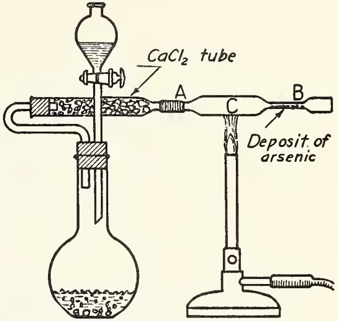


FIG. 15.—Testing for arsenic.

The substance under examination is now added to the generating flask, and if it contains arsenic a dark stain is produced in CB (caused by decomposition of arsine, AsH_3, into arsenic and hydrogen). The analyst has in his laboratory a number of standard tubes stained by the use of definite amounts of arsenious oxide (·001 mgm. for instance). By "matching" the stain produced in his test with one of his standard tubes, he can determine the amount of arsenic present.

Antimony

Occurrence and Extraction.—Antimony occurs in nature to a certain extent in the uncombined condition (*e.g.* in Queensland), but it is chiefly obtained as *stibnite,* Sb_2S_3. This substance is easily fused and so is separated from earthy material by *liquation* (i.e. heating, so as to make the fusible part flow away). The sulphide is then reduced in plumbago crucibles by heating it with iron

$$(Sb_2S_3 + 3Fe \rightarrow 2Sb + 3FeS).$$

The molten metal collects underneath the slag.

Properties.—Like phosphorus and arsenic, antimony is known in several allotropic forms, including a yellow, unstable variety which is slightly soluble in carbon disul-

phide (*cf.* phosphorus). As usually met with, however, antimony is a silvery-white metal of density 6·67, brittle, and easily powdered.

One of the chief uses of antimony depends on the fact that its alloys give very sharp castings. Whatever may be the explanation,[1] there is no doubt about the fact itself, and so antimony, alloyed with tin and lead, is much used for making printer's type. "Anti-friction metal," used for bearings, contains the same three elements. Pewter consists chiefly of tin alloyed with about 7 per cent. of antimony and smaller quantities of copper and bismuth.

Dilute sulphuric and hydrochloric acids have little or no action on antimony, but more concentrated acids cause hydrogen to be given off—

$$2Sb + 6HCl \rightarrow 2SbCl_3 + 3H_2,$$
$$2Sb + 3H_2SO_4 \rightarrow Sb_2(SO_4)_3 + 3H_2.$$

In these reactions antimony is obviously behaving like a metal. When heated with concentrated nitric acid it is gradually turned into a mixture of oxides. Remembering its metallic character, we should hardly expect the production of an acid corresponding to H_3PO_4 or H_3AsO_4, and indeed it is doubtful if antimonic acids exist at all, though some of their salts are known.

The hydride of antimony (stibine, SbH_3) has already been mentioned. As we should expect, it is quite devoid of basic properties. It is interesting to notice that in the experiment for detecting arsenic or antimony (Fig. 15), arsenic compounds give a stain only *beyond* the flame, while antimony compounds give a stain on both sides. This is due to the fact that stibine is more easily decomposed by heat than is arsine, as we should expect from the more pronounced metallic character of antimony.

[1] The explanation usually given is that such alloys expand on solidification, but it has recently been shown that in most cases they contract.

Bismuth

Occurrence and Extraction.—Bismuth occurs in the uncombined condition in Bolivia, Saxony, Australia, and some other regions, including British Columbia. The oxide *bismuthite* or *bismuth ochre* is also found.

From ores containing native bismuth the metal is obtained by liquation (*cf.* antimony). The ore is heated in sloping iron tubes, and the metal (which melts at the low temperature of 269°) easily flows away. From bismuth ochre, the metal is obtained by reduction with charcoal.

(*By courtesy of the Imperial Institute, London.*)

Refined bismuth from Tadanac, B.C.

Properties.—Bismuth is a reddish-white metal of density 9·80. It melts at 269° and boils at 1450°. Like antimony, it is brittle and easily powdered, and is largely used for making alloys, usually with lead and tin. These are peculiar in having very low melting points, often below 100°. *Rose's metal,* for instance, (bismuth 2, lead 1, tin 1) melts at 94°. Such "fusible alloys" as they are called have various uses. Thus, the end of a "sprinkler" pipe in a warehouse may be plugged up with one of them. If fire breaks out, the alloy melts and water is automatically released which extinguishes the fire.

Questions

1. " As we traverse the series nitrogen, phosphorus, arsenic, antimony, bismuth, we pass from elements of non-metallic character." Justify this statement by reference to (*a*) physical properties, (*b*) chemical properties.

2. In 1930 Canada imported 38·7 tons of phosphorus. Assuming that there was no waste, what weight of calcium phosphate, $Ca_3(PO_4)_2$, would be required to produce it?

3. In tabular form, compare the properties of red and yellow phosphorus. Your table should indicate (*a*) colour, (*b*) crystalline form, (*c*) specific gravity, (*d*) whether the variety glows or not, (*e*) solubility in CS_2, (*f*) tendency to take fire in air, (*g*) whether poisonous or not.

4. Red phosphorus contains a small amount of white phosphorus, present as an impurity. Suggest a method of purification.

5. A substance has the following percentage composition: sodium 21·7, hydrogen 1·9, phosphorus 29·2, oxygen 30·2, water of crystallization 17·0. What is its simplest formula?

6. Arsenopyrite sometimes gives off a garlic-like odour when struck with a hammer. How do you account for it?

7. The following results have been obtained for the vapour density of arsenic:—

Temperature	860°	1714°	1736°
Vapour Density	147	79	77

   If the atomic weight of arsenic is 75, what conclusions can we draw as to the number of atoms in the molecule?

8. Explain the chemical actions which take place on striking an ordinary match and a safety match, respectively.

9. You are provided with magnesium sulphate and any other necessary reagents. Explain how you could find whether a given substance was a phosphate.

CHAPTER VIII

COMPOUNDS OF SILICON AND BORON

Silicon

Occurrence.— Of the few miles of the earth's crust which men have been able to examine, silicon is the most abundant constituent with the exception of oxygen, being present to the extent of about 26 per cent. It is never found in the free condition, but its oxide, silica, SiO_2, is extremely abundant.

This oxide is found in several crystalline forms, the most important being quartz, or rock-crystal. Crystals of this, consisting of hexagonal prisms surmounted by pyramids,[1] are often met with. Sometimes they are very large, — occasionally as much as a yard or more in length—and one has been known to weigh nearly a ton.

By courtesy of the British Museum.

Quartz crystals.

Sand consists of small grains of quartz mixed with one or more other substances, the commonest being oxide of iron. In sandstone these are pressed together, the soft iron oxide acting as a sort of

[1] These crystals greatly interested the ancients. The Greeks thought they consisted of ice frozen so hard by the intense cold of the Alps that it was impossible to melt them. Hence they called the crystals *krystallos* (clear ice), a name which was later extended to include all crystalline substances.

cement to bind together the harder particles of quartz. In grey sandstone the soft material is often calcium carbonate.

So far we have spoken only of crystalline silica, but amorphous forms of this oxide are also found. *Kieselguhr* (or *diatomite*), for instance, consisting of the skeletons of tiny organisms known as diatoms, is almost pure silica. It is very porous and serves well as a filtering medium, *e.g.* in refining sugar. It is also used as a heat insulator, and as a constituent of concrete.

Flint is chiefly amorphous silica, but contains a little quartz. *Agate* is a somewhat similar mixture. On account of its hardness it is used for making the "knife-edges" of balances. Mortars and pestles that are to be used for grinding very hard substances are also sometimes made of agate.

We shall see presently that silica is an acidic oxide, and it is often found in combination with basic oxides as *silicates*. The commonest of these is ordinary clay (chiefly aluminium silicate). There are many others, among them being the minerals feldspar, asbestos, and mica.

It is interesting to note that considerable quantities of silica and silicates are being obtained in Canada. In 1930, well over 200,000 tons of quartz were obtained from quarries in Nova Scotia, Quebec, Ontario, and British Columbia. Diatomaceous earth is produced in Nova Scotia (about 1000 tons in 1931) and large deposits are now being developed in Ontario. Some is used for making dynamite, but its chief uses are as a sound and heat insulator, as a filtering medium, and as an admixture in concrete.

Mica and feldspar are also obtained in considerable quantities. Asbestos, a mineral of great importance to Canada, is considered on pp. 157-9.

Extraction.—Silicon is obtained at Niagara by heating a mixture of sand and coke in the electric furnace ($SiO_2 + 2C \rightarrow 2CO + Si$). As thus prepared, it is a hard, grey, crystalline substance somewhat resembling graphite in appearance. The melting point of silicon is very high (about 1420°). It is much used as a constituent of alloys, which

are very hard and possess great tensile strength. Alloys of iron and silicon are very resistant to the action of acids.

When heated in the air, silicon burns forming the dioxide. Under suitable conditions it combines with a number of other elements forming *silicides*. An important one is carbon silicide, — more often called silicon carbide, or *carborundum*,—much used as an abrasive on account of its great hardness. It is made at Niagara by heating a mixture of crushed coke, silver sand, and a little salt, saw dust being added to keep the mass porous. The equation for the main reaction is, $3C + SiO_2 \rightarrow SiC + 2CO$. The salt serves to remove iron present (as oxide) in the sand. It reacts with it forming ferric chloride, $FeCl_3$, which vaporizes.

Uses of Silica.—Some of these have already been mentioned. We may add that spectacle lenses ("pebbles") are often made from rock-crystal.

At a very high temperature silica can be softened like glass, and it can then be shaped into crucibles, flasks, etc. A remarkable property of such apparatus is that it can be made red hot and then suddenly cooled in water *without cracking*. This is owing to the fact that silica possesses a very low coefficient of expansion.

By far the most important use of silica, however, consists in the manufacture of glass, and we must now consider the chemical principles underlying this process.

Silica, an Acidic Oxide.—We must first understand that silica is an *acid-forming oxide*. Such oxides usually combine with water to form an acid (*e.g.* sulphur trioxide forms sulphuric acid). Silica does not do this — nothing happens, for instance, when sand is stirred up with water. But silicic acid may be obtained by other means, and when it is heated, silica is produced. In short, though it is *not* true that silica + water → silicic acid, it *is* true that silicic acid → silica + water.

Further, it is characteristic of an acidic oxide that it will combine with a basic oxide, forming a salt.

E.g. CO_2 (acidic oxide) + CaO (basic) → $CaCO_3$.

Now silica does combine with basic oxides, forming salts known as silicates, showing once again that it is an acidic oxide.

We said that silicic acid might be obtained "by other means". One method consists in slowly pouring a solution of sodium silicate into excess of hydrochloric acid ($Na_2SiO_3 + 2HCl \rightarrow 2NaCl + H_2SiO_3$). The liquid obtained is poured into a dialyser, a shallow vessel with a parchment bottom. This is floated on water. The sodium chloride and hydrochloric acid diffuse through the parchment into the water, and the silicic acid remains behind as a *colloidal solution, i.e.* it is divided into particles so small that they show not the least sign of settling to the bottom, and they cannot be stopped even by the finest filter paper. At the same time they are much larger than, say, the molecules of sugar present in a solution of that substance.

Colloidal particles are electrically charged (negatively in this case), something like ions. This causes them to repel one another, and so checks any tendency to coalesce into larger particles, which would "settle".

By suitable means the colloidal solution of silicic acid may be concentrated, and the molecules may be induced to group together or *polymerize.* The final product known as *silica gel* has some remarkable properties, no doubt due to the extreme smallness of the particles composing it (*cf.* activated carbon). Thus it readily absorbs gases, and was used in some of the gas masks during the Great War. It is used in industry for absorbing traces of hydrogen sulphide from other gases, for dehydrating the air used in blast furnaces, and for many other purposes.

Sodium Silicate. Glass.—We have already seen that when silica combines with basic oxides it forms silicates. Thus, if fused with sodium oxide, sodium silicate is produced ($Na_2O + SiO_2 \rightarrow Na_2SiO_3$). In practice, sodium *carbonate* is employed, the mixture being heated in a furnace. (See the first equation on the opposite page.) The product is dissolved in water under pressure, and the

familiar *water-glass* is thus obtained. It is much used for preserving eggs, its action depending on the fact that it seals up the pores of the shell and keeps air from entering. It is largely employed as a gum in the cardboard-box industry, and it has many other uses.

If silica is fused with a mixture of sodium carbonate and calcium carbonate, a mixture of sodium and calcium silicates is produced.

$$Na_2CO_3 + SiO_2 \rightarrow Na_2SiO_3 + CO_2$$
$$CaCO_3 + SiO_2 \rightarrow CaSiO_3 + CO_2.$$

This substance is the ordinary "soda glass" so much used in the laboratory. Window glass is similar, but it contains a larger amount of silica, which causes it to have a rather higher melting-point. Its composition is expressed roughly by the formula, $Na_2SiO_3 . CaSiO_3 . 4SiO_2$.[1] The green colour often seen in cheap bottle glass is due to the presence of silicate of *iron*. Remembering that sand usually contains oxide of iron, you can easily see how this particular silicate finds its way into the glass.

"Hard glass," used in the laboratory for combustion-tubes, etc., is made by using *potassium* carbonate instead of sodium carbonate, so that hard glass is a mixture, or compound,[1] of potassium and calcium silicates. Of the many other kinds of glass known,[2] a brief reference must be made to those ("Vita glass", "solarium glass", etc.) which have the property of transmitting a considerable percentage of the ultra-violet rays present in sunlight. They are now coming into use instead of ordinary window-glass. They are also used as containers for foods which are being "irradiated", *i.e.* exposed to ultra-violet rays with a view to the production in them of vitamin D. Apparently the

[1] It is very difficult to say whether the various kinds of glass are to be regarded as *mixtures* of silicates with one another and with silica, or as highly complex *compounds* of these substances—compounds of compounds, so to speak.

[2] Some of the modern glasses often contain other acidic oxides, *e.g.* "Pyrex" glass contains borates rather than silicates.

making of such glass is not so much a question of a special formula, but rather of purity of materials and refined methods. Iron oxide, for instance, must be eliminated as completely as possible.

Glazing consists in the depositing of a thin film of glass over a surface, usually with the object of making it non-porous. You can illustrate the process by taking equal parts of litharge (PbO) and anhydrous sodium carbonate and mixing into a cream with water. A bit of plant pot covered with this and baked in a muffle furnace, or in the middle of a good fire, is soon glazed. If a small quantity of cobalt nitrate is added to the mixture, the glaze will be blue, owing to the formation of cobalt silicate.

The process of *enamelling* is in some respects very similar to glazing. The mixture used is, however, rather more complex, and instead of the glass being actually made on the surface of the article, it is prepared independently. It is allowed to solidify, ground up with water, and applied as a very thin coating to the article being treated. After being allowed to dry, it is heated sufficiently to cause it to flow over the surface.

In the manufacture of articles such as tiles, drain-pipes, etc., a cheap glaze is produced by throwing salt into the kiln. At the existing high temperature the salt is converted into vapour and is hydrolysed (p. 50) by the water vapour present:— $NaCl + H_2O \rightarrow NaOH + HCl$. The caustic soda thus produced then reacts with the silica and alumina of the pottery, forming a sodium-aluminium silicate which serves as a glaze.

Glass-making and glass-blowing are very ancient industries, as is proved by the fact that coloured glass beads have often been found interred with Egyptian mummies. The illustration apparently represents two of these primitive glass-blowers. It is taken from an Egyptian tomb-painting of date about B.C. 2000, but opinion is divided as to whether the industry represented is glass-blowing or a primitive method of copper smelting.

Of late years there have been great advances made in the manufacture of glass, and perhaps some day we shall see really unbreakable glass. Already one firm advertises a flask with which it is possible to drive a 1½ inch nail up to the head into soft wood!

By courtesy of "Oil-Power."

An ancient Egyptian industry.

Complex Silicates.—So far we have referred to silicic acid as though it corresponded exactly to carbonic acid (H_2SiO_3 and H_2CO_3), and to silicates as though they corresponded to carbonates.

Silicates, however, are often extremely complex. Common clay, for instance, is chiefly aluminium silicate $Al_2Si_2O_7 . 2H_2O$ ($=Al_2O_3 . 2SiO_2 . 2H_2O$), but a discussion of the formulae of complex silicates is beyond the range of this book.

The yellowish colour of clay is due to the presence of oxide of iron, Fe_2O_3. When this is not present, we have a white clay,—kaolin or china clay.

As we shall see presently, clay is a substance used in a number of important industries, *e.g.* the making of bricks, pottery and cement, so we must look a little further into its properties.

Clay is said to be in the *colloidal* condition, because it consists of the extremely fine particles of which we have already written in connection with silicic acid. The par-

ticles of aluminium silicate in the clay have a feeble negative charge, and so they repel one another. This repulsion, however, is too feeble to overcome the cohesion between the particles, with the result that on the whole they stick well together, as we are reminded when we work a bit of clay between our fingers. Further, the particles of iron oxide present in ordinary clay are *positively* charged, and no doubt serve as centres of attraction for the negatively charged silicate particles.

When clay is heated to a temperature not exceeding 100°, any adhering moisture is driven off. The substance becomes dry and hard, but if cooled and mixed with water it becomes plastic as before. If, however, the temperature is raised much beyond 100°, the *combined* molecules of water—the " $2H_2O$ " in the formula—are expelled, and on cooling and mixing with water the substance does not again become plastic,—it remains porous.

Men farming small plots of clay soil occasionally "burn" it cautiously, gathering the clay into heaps, which are banked in so that the fire cannot get beyond the smouldering stage. The temperature must be well above 100°, but much below that at which the clay would become of brick-like hardness. The material is now returned to the soil,—it is porous and can easily be broken up.

Let us consider very briefly some of the industries in which clay is employed.

Brick-making. Most of the processes here are too familiar to need description. It is worth noting, however, that sometimes a little caustic soda is added to the " clay slip " (*i.e.* the mixture of clay and water ready for moulding). This causes the negative charge on the particles to be increased, and they repel one another more strongly, with the result that the clay can now be poured into moulds. Thus, it is not necessary to add so much water, which would later have to be driven off again at the cost of additional fuel.

The bricks are heated to about 950°C. If heated much beyond this temperature the materials soften and the brick assumes a glassy appearance and is said to be vitrified The red colour is due to the presence of the oxides of iron already mentioned.

Drain tiles and other crude products are made in the same way. If a glaze is required, salt is added and acts as already described.

Firebrick is required for making furnace linings, crucibles, the large retorts in gas-works, etc., and must be able to resist a temperature of 1500°C. without softening. Hence a specially selected clay is used,—rich in oxides of silicon and aluminium, but with as little as possible of the oxides of calcium, iron, etc., which would cause the product to contain a rather easily fusible silicate. Suitable clays for firebrick are found in various parts of Canada, and notably in south-west Saskatchewan.

China. For this a pure clay free from compounds of iron is required. Sometimes a fairly pure natural clay can be found (china clay), and by suitable treatment with water the iron compounds are washed out.

In the Schwerin method of purification the clay is mixed up with water and electrodes are introduced. The positively charged iron oxide particles move to the cathode, while the negatively charged silicate particles move in the opposite direction, and the white aluminium silicate is thus obtained in a pure condition.

Feldspar is now added to the purified clay to render it more fusible, after which the articles are moulded into the desired shapes and then fired. After this first firing they are porous, and have to be glazed as described on p. 95. The articles have now (usually) to be decorated. The required patterns are inscribed on them, oxides being employed which will give silicates of suitable colour. On fusing once more, these oxides react with the glaze, and the necessary coloured silicates are produced.

The procedure in making *porcelain* is much the same, but a less fusible silicate is employed in the first instance. For common table pottery the clay employed is not so pure, and it is not heated to such a high temperature.

By courtesy of the Portland Cement Association.
Old time vertical kiln. This pioneer burner used coke for fuel. The charge was arranged in alternate layers of powdered rock made into bricks.

Cement. The materials required for making cement are limestone and clay. Occasionally these are found together in nature in just the right proportions, but usually they are obtained separately, and after being intimately mixed they are "burned", a higher temperature being employed than in lime burning. When the mixture begins to fuse it is cooled forming a "clinker". This when ground up with about 3 per cent. of gypsum forms "Portland Cement".

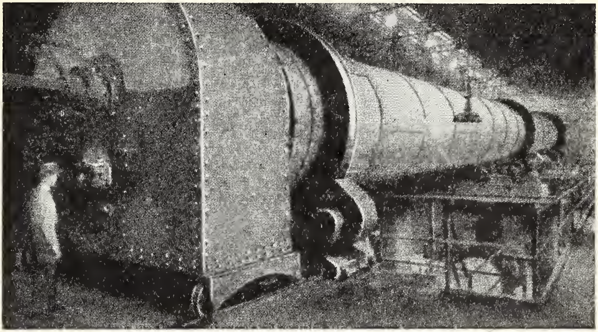
The old-fashioned cement kilns were practically lime-kilns of what is known as the "discontinuous" type. In modern practice a rotary kiln is employ, and at Port Colborne (Ontario), one of these has just been installed with a length of 410 feet,—the largest in the world. These rotary kilns are heated with a great tongue of flame, usually fed by a continuous blast of coal-dust, but in some districts where oil and natural gas are plentiful, these are used instead of coal-dust.

Cement possesses the very curious property of setting under water. The reason for this is not known with certainty, but appears to be somewhat as follows.

The cement contains tricalcium silicate, $(CaO)_3 . SiO_2$, and tricalcium aluminate, $(CaO)_3 . Al_2O_3$. In the presence of water the former undergoes no change, but the latter is acted upon thus—

$$(CaO)_3 . Al_2O_3 + 6H_2O \rightarrow 3Ca(OH)_2 + 2Al(OH)_3.$$

The calcium hydroxide gradually crystallizes out, binding together the minute particles of tricalcium silicate, while



By courtesy of the Portland Cement Association.

Modern rotary kiln. The pulverized raw mix goes into the rotary kiln, where it is burned to cement clinker—glass hard pebbles the size of marbles. Powdered coal is blown through the tube at the left, burning with a temperature ranging from 2,500° to 3,000°F.

all the little spaces in between are filled up by the aluminium hydroxide. The result is that a thoroughly impervious mass is produced. Better results are secured when the action proceeds slowly, and here the gypsum (already mentioned) assists by acting as a *negative* catalyst, *i.e.* one which retards the speed of a chemical action.

Canada now manufactures practically all the cement she needs—some ten million barrels per year—yet in 1891 cement was actually being brought from England to British Columbia in sailing ships that had to make the tedious journey around Cape Horn.

Boron

Boron occurs in nature in several compounds, an important one being sodium borate (strictly *pyroborate*) or **borax**, $Na_2B_4O_7 . 10H_2O$. This is rather widely distributed,

and in California there is actually a lake (Lake Borax) whose bed is a mass of the crystallized substance, sufficiently pure to be marketed with little or no further treatment. Crystals are often found weighing a pound or so, and as much as seven inches long.

The calcium salt known as *colemanite*[1] is also found. There is no commercial use for this as such, but it is ground to a powder and boiled up with a solution of sodium carbonate, when by double decomposition we obtain calcium carbonate and sodium borate. The solution is filtered and allowed to crystallize out.

Borax has many domestic and other uses. It is used in ironing for giving a gloss to linen, and as a flux in soldering. Then, it is the source of the borates which, as we have already seen, are added to silicates in making some of the newer kinds of glass. Similarly, it is often employed (usually with silicates) in the preparation of glazes.

In the laboratory we use it for "borax bead tests". When heated on a platinum wire it swells up, loses its water of crystallization, and finally melts to a clear glassy bead. In some cases salts when heated in this bead give it a charasteristic colour, *e.g.* copper salts give a blue colour, and chromium salts a green one. The reactions are

(*a*) At the high temperature, the salt decomposes leaving the basic oxide, *e.g.*, $CuSO_4 \rightarrow CuO + SO_3$.

(*b*) This reacts with the borax giving a *metaborate* (the borax also being converted into sodium metaborate),

$$CuO + Na_2B_4O_7 \rightarrow Cu(BO_2)_2 + 2NaBO_2.$$

(N.B.—Borax or sodium pyroborate may be regarded as $Na_2O . 2B_2O_3$ and sodium metaborate as $Na_2O . B_2O_3 \rightarrow 2NaBO_2$. *Cf.* foot-note.)

On p. 50 we saw that sodium carbonate is slightly hydrolysed in solution into sodium hydroxide and car-

[1] $Ca_2B_6O_{11} . 5H_2O$. We may write $Ca_2B_6O_{11}$ as $(CaO)_2 . 3B_2O_3$. Boron reminds us of silicon in its tendency to form complex salts produced by the combination of its oxide with varying proportions of basic oxides.

bonic acid ($Na_2CO_3 + 2H_2O \rightleftharpoons 2NaOH + H_2CO_3$), and it was explained why the solution was alkaline. Very similar remarks apply to a solution of sodium borate. It hydrolyses to some extent, giving sodium hydroxide and boric acid,[1] and the solution is alkaline because sodium hydroxide is a strong base, throwing plenty of hydroxide ions into solution, while boric acid is a weak acid, yielding very few hydrogen ions.

Boric Acid.—There are several boric acids produced by the combination of boron trioxide with water in different proportions. Ordinary boric acid or *orthoboric* acid is H_3BO_3 (corresponding to $3H_2O + B_2O_3 \rightarrow 2H_3BO_3$). *Metaboric* acid HBO_2 corresponds to $H_2O + B_2O_3$, and *pyroboric* acid, to $H_2O + 2B_2O_3$.

Much the most important acid is the orthoboric, H_3BO_3. It is the " boric acid " or " boracic acid " often used for cleansing wounds, etc. People who have used it will know that it dissolves fairly easily in hot water but only slightly in cold. As an acid it is very weak, only turning litmus to a sort of uncertain red and having no effect at all on methyl orange.

It is prepared by adding concentrated hydrochloric or sulphuric acid to a hot saturated solution of borax. On cooling, crystals are deposited.

$$Na_2B_4O_7 + H_2SO_4 + 5H_2O \rightarrow Na_2SO_4 + 4H_3BO_3$$

When heated, orthoboric acid loses the elements of water in successive stages. At 100° it is converted into metaboric acid ($H_3BO_3 \rightarrow H_2O + HBO_2$), and at 140° into pyroboric acid ($4HBO_2 \rightarrow H_2B_4O_7 + H_2O$). When strongly heated, this is converted into a glassy mass of boron trioxide or boron anhydride ($H_2B_4O_7 \rightarrow H_2O + 2B_2O_3$).

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[1] The boric acid produced is not $H_2B_4O_7$, but H_3BO_3, and this complicates the equation, which is

$$Na_2B_4O_7 + 7H_2O \rightleftharpoons 2NaOH + 4H_3BO_3.$$

It is given here for reference, but need not be learnt.

Questions

1. If common red sand is boiled for a few minutes with hydrochloric acid, a reddish-yellow solution is obtained, and a grey residue settles to the bottom of the test-tube. How do you account for these results?

2. It is said that glass was first made accidentally by some Phœnician sailors who made a fire on the sandy shore of the Levant, and used lumps of soda (from their cargo) as a stand for their cooking-pot. Discuss the possibility of glass having been produced in this way.

3. Robinson Crusoe made earthenware vessels from clay, but did not know how to glaze them. How might he have tackled the problem?

4. Makers of silica crucibles advise their customers not to heat strong alkalies in them. Why?

5. What is the chief difference between kaolin (china clay) and common clay?

6. Can you account for the fact that clay is so impervious to moisture?

7. A clayey soil is usually much easier to work after it has been treated with lime. Why?

8. Common clay would be an excellent source of aluminium if a cheap means of extraction were available. Assuming that common clay contains 40 per cent. of aluminium silicate, what weight of aluminium is contained in 100 tons of it?

9. Find the empirical formula of a substance having the following percentage composition:—potassium, 14·0; aluminium, 9·7; silicon, 30·2; oxygen 46·1.

10. What points of resemblance can you find between boron and silicon? Having regard to their position in the periodic table, why would you expect some resemblance?

11. In what respect is the method given on p. 103 for the preparation of boric acid similar to those employed for preparing nitric acid and hydrochloric acid?

12. Can you suggest why borax, used in ironing, should give a gloss to linen?

CHAPTER IX

METALS AND ALLOYS

Most people in a rough sort of way can distinguish between " metals " and " non-metals ". They would decide, for instance, that copper, silver, and lead are metals, and that charcoal, sulphur, and oxygen are non-metals. If we asked them how they distinguished between the two classes they would most likely answer that a metal has a peculiar " shine " or lustre that a non-metal does not possess.

That is, in fact, a useful means of distinguishing. We might notice a few others. Metals are usually good conductors of heat and electricity, while non-metals are not. A piece of sulphur conducts heat so badly that if you hold a roll of it firmly in your warm hand you can hear it cracking. You can easily reason out for yourself why this little experiment proves that sulphur is a bad conductor of heat.

Metals are often " sonorous ", *i.e.* they give out a ringing sound when struck. They usually have a high melting-point, and in fact only one of them (mercury) is a liquid at ordinary temperatures. Those non-metals that are solid at ordinary temperatures (*e.g.* sulphur and phosphorus) usually have low melting-points, and many non-metals (oxygen and nitrogen, for instance) have boiling-points so low that at ordinary temperatures they are gases. Metals usually have a rather high density and non-metals, a low one. Metals are more or less malleable and ductile, while non-metals are brittle.

You can easily think of exceptions to the rules just mentioned. Graphite " shines ", for instance—that is why it is used for blackleading stove tops and lids. Lead is not

sonorous, charcoal has an extremely high melting-point, and sodium has a density so low that it will float on water. At the same time the distinctions we have mentioned hold good in the majority of cases.

Chemical Differences.—The points we have discussed so far are all concerned with *physical* properties. We must now consider the *chemical* properties which distinguish metals from non-metals.

Much the most important is that *metals give rise to basic oxides, non-metals to acid-forming oxides.* We shall not say much more about this, because it will already have been discussed earlier in the course.

Closely connected with the general rule that,

$$\textit{basic oxide} + \textit{acid} \rightarrow \textit{salt} + \textit{water},$$

is the fact that, in many cases,

$$\textit{metal} + \textit{acid} \rightarrow \textit{salt} + \textit{hydrogen}.$$

If you write out the equations for the action of sulphuric acid on zinc oxide and on zinc respectively, you will see quite clearly what is meant. Hydrogen is not given off, however, in the case of those metals, such as copper, which are below hydrogen in the electromotive series (p. 51).

Besides the oxides, there are two other groups of compounds which are well worth considering in our comparison of metals and non-metals. They are the *chlorides* and the *hydrides.* Chlorides of metals are not as a rule much hydrolysed by water, while with chlorides of non-metals the reverse is the case (*e.g.* $PCl_3 + 3H_2O \rightarrow H_3PO_3 + 3HCl$).

Non-metals usually form stable compounds with hydrogen. Thus, water (H_2O), ammonia (NH_3), hydrogen sulphide (H_2S), hydrogen chloride (HCl), and methane (CH_4) are the hydrides of oxygen, nitrogen, sulphur, chlorine, and carbon respectively. These hydrides are either gases, or liquids which can easily be vaporized. They are not decomposed by water.

Metals seldom form stable hydrides. When they do, the hydrides are solids decomposed by water. Thus, calcium forms a solid hydride CaH_2, which is readily decomposed by water giving hydrogen—

$$CaH_2 + 2H_2O \rightarrow Ca(OH)_2 + 2H_2.$$

(Under the name *hydrolith,* this hydride has sometimes been used as a source of hydrogen for filling balloons, etc.)

Finally, *electrolysis* enables us to classify most of the elements as metals or non-metals. Metals are electropositive, and may be deposited *alone* at the cathode. A non-metal never appears at the cathode except, occasionally, *in conjunction with some other element* (*e.g.* if a solution of ammonium chloride, NH_4Cl, were electrolyzed, the non-metal nitrogen would appear at the cathode, but it would be in conjunction with the hydrogen).

Alloys.—If two (or more) metals are fused together, the liquid obtained appears to be homogeneous, *i.e.* the same all through; the metals seem to mix perfectly. Such a mixture is known as an **alloy**. A very common example of an alloy is brass, made from copper and zinc, and another is solder, consisting of tin and lead. No doubt when brass is made, the copper dissolves in the molten zinc, or we may say equally well that the zinc dissolves in the molten copper. The brass when solidified is known as a **solid solution.**

Although one molten metal will usually dissolve freely in another, there are plenty of exceptions. Thus, 100 gm. of molten lead will dissolve only 1·6 gm. of zinc, and 100 gm. of zinc will dissolve only 1·2 gm. of lead, so for all practical purposes we may say that a lead-zinc alloy does not exist. Again, mercury readily dissolves most metals forming alloys known as **amalgams,** but it does not directly form an amalgam with iron. That is why mercury when being dealt with on the large scale is packed in iron bottles.

The " solid solution " kind of alloy can usually have any composition we please to give it. Thus " coarse solder " contains two parts of lead and one of tin, but " fine solder " contains two parts of tin and one of lead. Some alloys, however, have been shown to be chemical compounds with a perfectly definite composition. Magnesium and tin, for instance, form a compound having the composition Mg_2Sn.

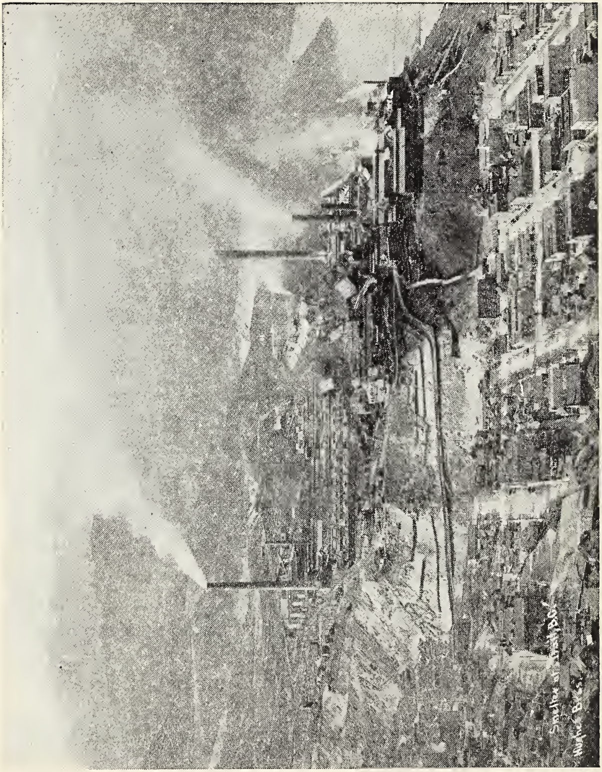
The most ancient of the alloys is bronze. Perhaps, long centuries ago in ancient Egypt, some smith accidentally put a quantity of scrap tin into a vessel already containing copper. He melted the mixture and obtained a substance with such useful properties—great hardness, for instance—that it came to be very widely employed and actually gave its name to the Bronze Age. The physical properties of bronze are by no means the " average " of those of copper and tin, and this deviation of physical properties is found in many other cases. Thus a " cast iron " has been prepared which is actually non-magnetic. It contains 85% of iron alloyed with 15% of manganese and nickel. Conversely a magnetic alloy is known consisting only of manganese, copper, and aluminium, all non-magnetic elements. Then, nickel and iron in common with almost all other substances, expand by a definite amount when heated. Yet a nickel-steel alloy can be prepared which has a practically zero expansion over a considerable range of temperature, and so is of great use in making, for instance, the pendulums of clocks required to keep particularly exact time. In your electricity studies you may have learnt that the electrical resistance of a metal nearly always increases with the temperature. Now, in a resistance box it would be extremely inconvenient if the standard resistances varied from one day to another, and this is avoided by using *manganin* wire. Manganin is an alloy of manganese and copper, and though the resistance of each of these metals increases with temperature, that of the alloy is constant. The fact is that alloys can be prepared possessing all sorts of properties which are shown by no single metal, and so

men are devoting a great deal of time to the study of the subject.

Extraction of Metals.—The methods by which metals are extracted from their ores differ very much according to the metal concerned and also according to the nature of the ore. The process by which copper is obtained from copper oxide, for instance, is quite different from that by which it is obtained from the sulphide. Certain processes, however, are of fairly general application, and these are well worth considering.

First of all there is the *Flotation,* or *Froth-flotation* process, used in the preparation of the ore for the smelter. Ore as taken from the earth often contains only a very small proportion—2 per cent., perhaps—of the mineral required, the rest being earth, rock-material, etc. known as *gangue.* First of all the ore must be concentrated by the removal of as much as possible of this gangue. To achieve this result, it was formerly crushed and washed with water, the gangue separating from the mineral owing to its different specific gravity (the gold-digger formerly separated gold-dust from sand, etc. in much the same way). This method of separation was not very satisfactory, for when the mineral was afterwards smelted, the amount of metal finally obtained was seldom as much as 70 per cent. of what was originally present in the ore.

The froth-flotation process brought about a great improvement. It depends chiefly on the fact that even quite heavy particles will float on water provided the liquid does not wet them,—as in the familiar game of making a needle float. The ore is finely crushed and mixed with water, to which is added a very small amount of a suitable oil. Eucalyptus oil is often used, about 2 lb. to every ton of water. Air is now blown in freely to produce a good froth, and the mineral particles rise to the surface with the bubbles. The oil seems to act partly by assisting in the formation of bubbles, partly by making the mineral particles very slightly " greasy " so that they are less liable to be made



Smelter at Trail, B.C. *By courtesy of Consolidated Mining and Smelting Co.*

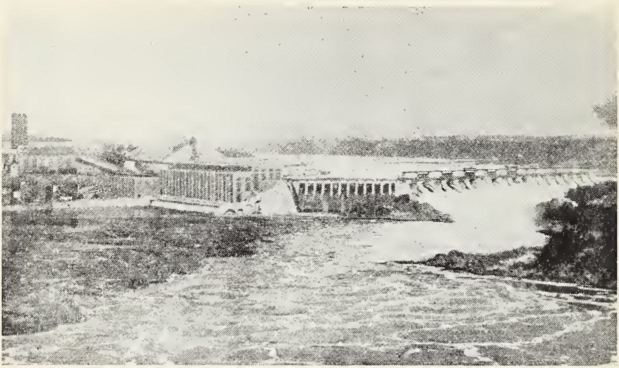
wet by contact with the water. It is found that the particles of gangue (earthy material, etc.) become wet and sink. To assist in producing this wetting a little sulphuric acid is sometimes added. With the flotation process the yield of metal is increased from the old figure of 70 per cent. (at the most) to 90 or 95, and many low-grade ores are being treated which in the days of the older process had been rejected entirely. After the gangue has been more or less completely removed, the mineral is smelted, but it often undergoes a preliminary process known as *roasting.* This consists in heating it in such a way that a chemical action occurs in which air takes part. Zinc ores, for instance, often contain both sulphide and carbonate. On roasting, both of these give rise to the oxide:—

$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2;$$
$$ZnCO_3 \rightarrow ZnO + CO_2.$$

The zinc oxide is then ready for the further processes described on p. 160.

Electrical Methods are also somewhat generally—and increasingly—used in the extraction of metals. In some cases, the purified ore (mixed with a flux) is subjected to electrolysis, as in the case of aluminium (p. 168). More often a solution of a salt of the metal is employed, as in the production of "electrolytic copper" (p. 199). It is worth noting that for the metals high in the electromotive series—potassium, sodium, calcium, aluminium, etc.—the electrolytic method is almost the only one by which extraction is possible. For this reason, such metals as those just mentioned were discovered only very late in the history of civilization.

The production of metals by electrical methods requires cheap current, and this in turn depends on plenty of water power being available. In this respect, Canada is particularly well placed. Thus, the Ontario Hydro-Electric Commission, controlled by the Provincial Government, has installed a power-plant at Niagara Falls with a capacity of well over half a million horse-power, and is distributing

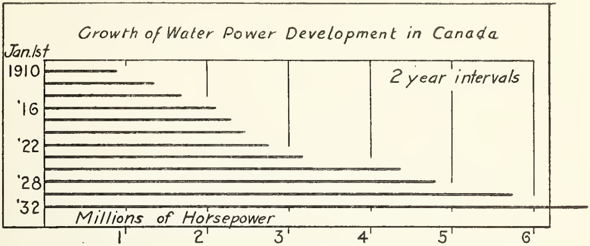


By courtesy of the Shawinigan Water and Power Co.
Water power in harness — Grand'Mere on the St. Maurice River. This power plant has a capacity of 189,000 h.p., and steel tower transmission lines, operating at 60,000 volts, run from it to Quebec, Shawinigan Falls, etc.

current throughout the province at about the cost of production. British Columbia is developing its metal industries with cheap electric power derived from its rivers, and, in Alberta, the Calgary Power Company has just completed a 132,000-volt transmission line from the Ghost development on the Bow River to Calgary. These are fairly typical examples. Canada as a whole has now about seven million horse-power derived from its rivers and lakes, though of course this energy is used for many purposes other than the extraction of metals.

With its vast resources in almost every kind of ore and its great supplies of hydro-electric power, it is not surprising that Canada's output of metals is both large and increasing. Some idea of the progress already made will be obtained from the accompanying graph, but with the ever increasing demand for metals and alloys, it is difficult even to guess at what the future has in store.

[For **Questions** see p. 126.]



(*By courtesy of the Dominion Bureau of Statistics.*)

FIG. 16.—Development of water power.

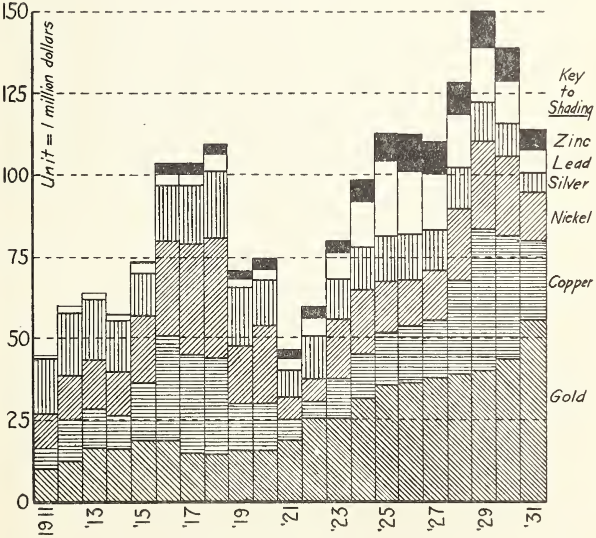


FIG. 17.—Value of chief metals produced in Canada, 1911 - 1931.

CHAPTER X

SODIUM AND ITS COMPOUNDS

Family Characteristics.—Sodium is one of a family of metals (Group I, family A) consisting of lithium, sodium, potassium, rubidium, and caesium. If we set down a few of their properties in tabular form we shall see that these change with considerable regularity as the atomic weight changes.

	Lithium	Sodium	Potassium	Rubidium	Caesium
Atomic weight	7	23	39	85	133
Density at 0°	0·59	0·97	0·86	1·53	1·90
Melting point	186°	98°	62°	39°	28°
Boiling point	1609°	883°	762°	700°	670°

After being exposed to the air for only a second or two, the silvery surface of freshly-cut sodium is found to be tarnished. Potassium tarnishes even more rapidly, but with lithium the action is rather slower than with sodium. Rubidium and caesium oxidize so rapidly that if a fragment of either of these metals is exposed to the air it takes fire spontaneously.

All five metals act upon water producing the hydroxide of the metal together with free hydrogen, *e.g.*

$$2Na + 2H_2O \rightarrow 2NaOH + H_2.$$

Here again, the action takes place with increasing vigour as the atomic weight increases. We may sum up the situation fairly well by saying that with increasing atomic weight these elements become more and more electro-positive (p. 50), and, in fact, caesium is the most electro-positive element known.

All the elements are univalent, forming salts of the type RCl, R_2SO_4, etc. (*e.g.* NaCl, Na_2SO_4, etc.).

The " compound radical " ammonium, NH_4, has never been isolated. However, its compounds are in many respects so similar to those of sodium, potassium, etc. that ammonium is usually dealt with as though it actually belonged to the family.

Sodium is much too high in the electromotive series to be obtained by any of the usual smelting processes. It is actually obtained by electrolysis of the *fused* hydroxide, NaOH, sodium and hydrogen appearing at the cathode and oxygen at the anode.

It is a soft metal—easily cut with a knife—and so light that it will float on water. As already mentioned, when freshly cut it is bright like silver, but in two or three seconds it becomes tarnished owing to oxidation. Owing to the fact that it combines so readily with oxygen, sodium is always kept under some liquid which does not contain that element (*e.g.* kerosene or gasoline, both of which are mixtures of hydrocarbons).

Sodium Chloride.—We mention this compound first because it occurs on such a large scale in nature. You will already have studied its chief properties, and here we shall add only one point—*i.e.* it does *not,* when pure, absorb atmospheric moisture, in spite of the fact that the domestic supply is often found to " cake ". This caking is due to the presence of small quantities (less than 1 per cent.) of magnesium and calcium chlorides, which are very deliquescent. Patent table salts, guaranteed to keep their fine powdery form, are sometimes prepared by adding a calculated quantity of sodium bicarbonate. This reacts with the calcium chloride (and similarly with magnesium chloride)—

$$CaCl_2 + 2NaHCO_3 \rightarrow CaCO_3 + H_2O + 2NaCl + CO_2.$$

The only impurities present in the table salt are, therefore a little calcium carbonate (or powdered chalk), which

does not absorb moisture, and the very similar magnesium carbonate.

Sodium Hydroxide, NaOH, is now mostly prepared from brine by electrolysis; something is said about this on pp. 44-5. An older method of preparation is still employed to a certain extent, and consists in boiling slaked lime with sodium carbonate—

$$Ca(OH)_2 + Na_2CO_3 \rightarrow 2NaOH + CaCO_3.$$

The process is easily illustrated in the laboratory, and it is complete when, after allowing the insoluble material to settle, a small quantity of the clear liquid no longer effervesces with hydrochloric acid. This indicates, of course, that all the sodium carbonate has been used up. If a fairly generous excess of slaked lime is used, the small scale reaction is complete in five or ten minutes.

Sodium hydroxide, usually bought in the form of white sticks, is a very deliquescent substance (notice how a stick of it " sweats " after even a few seconds' exposure to the air). It is, therefore, sometimes used for drying gases—especially ammonia, which reacts with the more usual drying agents.

As is usually the case with a deliquescent substance, it is extremely soluble in water. Much heat is produced at the same time. The solution is strongly alkaline to litmus. It feels slimy, and has a corrosive action on the skin, filter paper, etc.,—hence the common name " caustic soda ".

Sodium hydroxide is an excellent example of a base, for it easily reacts with an acid, producing a salt and water only. With hydrochloric acid, for example, we have—

$$NaOH + HCl \rightarrow NaCl + H_2O.$$

As it reacts so readily with acids, it is not surprising to find that it also reacts with anhydrides (*i.e.* acid-forming oxides). Thus, it quickly absorbs carbon dioxide, and it is sometimes used in the laboratory for removing carbon dioxide from a mixture of gases,—

$$2NaOH + CO_2 \rightarrow Na_2CO_3 + H_2O.$$

If we continue to pass in carbon dioxide after all the hydroxide has been turned into carbonate, the *bicarbonate* is formed. This remains in solution.

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3.$$

With sulphur dioxide (*i.e.* sulphurous anhydride) the action is similar, sodium sulphite, Na_2SO_3, being first formed, and later sodium bisulphite, $NaHSO_3$.

Closely connected with this tendency to react with an acidic oxide, is the well-known fact that the stopper of a bottle containing sodium hydroxide solution is often found to be stuck fast. This is chiefly because of the action of the solution on the silica contained in the glass, the stopper being united to the bottle by a continuous layer of sodium silicate—

$$2NaOH + SiO_2 \rightarrow Na_2SiO_3 + H_2O.$$

It is worth noting that the only elements which form *soluble* hydroxides are those near the top of the electromotive series, *i.e.,* (so far as we are concerned) potassium, sodium, and calcium, the last being only slightly soluble. The radical ammonium, NH_4, also forms a soluble but very unstable hydroxide.

Hence, as a general rule, when sodium hydroxide is added to a solution of a salt of some other metal, the hydroxide of that metal, being insoluble, is *precipitated.* On adding it to a solution of ferric chloride, for instance, ferric hydroxide appears as a brown precipitate—

$$FeCl_3 + 3NaOH \rightarrow 3NaCl + Fe(OH)_3.$$

If we add a solution of sodium hydroxide to an ammonium salt, ammonia is produced, especially on warming. This is owing to the fact that ammonium hydroxide is so unstable.

$$\begin{aligned} NH_4Cl + NaOH &\rightarrow NaCl + NH_4OH \\ &\rightarrow NaCl + NH_3 + H_2O. \end{aligned}$$

Caustic soda is largely used in the manufacture of soap, rayon, wood-pulp, paper, and a great many other products.

Oxides.—Sodium forms several oxides, the most important being the peroxide, Na_2O_2, a pale yellow substance frequently used in the laboratory as an oxidizing agent. It is made by passing a current of purified air, at 300°C., through iron tubes containing aluminium trays on which sodium has been placed. When it is acted upon by carbon dioxide, oxygen is produced ($2Na_2O_2 + 2CO_2 \rightarrow 2Na_2CO_3 + O_2$). Hence it has sometimes been used for purifying the air in enclosed spaces such as submarines.

Oxygen is also produced by the action of water on sodium peroxide [$2Na_2O_2 + 2H_2O \rightarrow 4NaOH + O_2$], and this reaction is sometimes used when small supplies of oxygen are needed for medical or other purposes. The sodium peroxide is bought in small sealed tins under the name of "oxone". When oxygen is required, one of these tins is perforated at several points and placed in an apparatus shown diagrammatically in Fig. 18, where the water is indicated by shading. On opening the valve V, water rises into the inner vessel A and enters the " oxone " tin through the perforations at the bottom. Oxygen is now given off as long as required, but on closing the valve the pressure rises and soon drives back the water to a level below that of the bottom of the perforated tin.

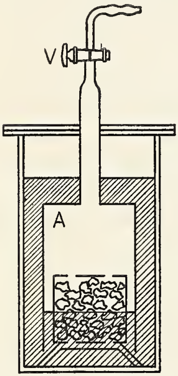


Fig. 18.—Oxygen from Sodium Peroxide.

Sodium Nitrate.—This substance occurs naturally in Chile, whence its commercial name "Chile saltpetre". The deposits cover an area of about 344 sq. miles in a desert region in the north of the country. The district is nearly rainless—in fact, as sodium nitrate is very soluble in water, it is evident that it would long since have been washed out of the soil if there had been any great amount of rain. Nobody knows for certain how the deposits were formed.

The "caliche", as the crude substance is called, is usually

found a few feet below the surface. Bore-holes are made and gunpowder or dynamite cartridges introduced. The explosion makes the caliche far more accessible. It is then crushed and treated with boiling water, the insoluble constituents (sand, etc.) being allowed to settle. After this, the solution is run into large pans in which the sodium nitrate crystallizes out as the liquid cools.

The export of the substance began in 1830 with 1000 tons, and had risen by 1911 to about 2½ million tons, a figure at which it tends to remain roughly constant. The world's demand for nitrates has been increasing rapidly, as you can see from the graph on p. 136. That increase, however, is being met chiefly by the production of "synthetic" products as explained in Chapter XII. Until recently, the Chilean Government was raising something like three-quarters of its entire revenue by levying a tax on every ton of nitrate exported, so it must view the production of synthetic nitrates with a good deal of concern.

Owing to the shape of its crystals, sodium nitrate is sometimes known as "cubic nitre". It is rather hygroscopic, and for that reason cannot be used as a substitute for potassium nitrate in the manufacture of gunpowder. Most of the world's supplies of potassium nitrate, however, are now obtained from Chile saltpetre and potassium chloride. Some account of the process is given on p. 130 in connection with potassium nitrate.

When strongly heated, sodium nitrate melts and gives off oxygen, leaving the *nitrite* ($2NaNO_3 \rightarrow 2NaNO_2 + O_2$). In the laboratory, it is frequently used in the preparation of nitric acid, which is produced on heating it with sulphuric acid.

$$NaNO_3 + H_2SO_4 \rightarrow NaHSO_4 + HNO_3.$$

It is used on a large scale for the same purpose, but an increasing amount of the nitric acid of commerce is now being made by other methods.

Sodium Carbonate, Na_2CO_3, is manufactured on a large scale by what is known as the Solvay or Ammonia-Soda process. This depends on the fact that if a solution of

ammonium bicarbonate is added to strong brine, sodium bicarbonate separates out—

$$NH_4HCO_3 + NaCl \rightleftharpoons NH_4Cl + NaHCO_3.$$

The arrows indicate that the process is reversible, but by carefully regulating the conditions (especially temperature which is kept near 40°C.) about two-thirds of the sodium chloride undergoes the desired change.

Ammonium bicarbonate is not actually used in practice, ammonia, carbon dioxide, and water being used instead ($NH_3 + H_2O + CO_2 \rightarrow NH_4HCO_3$). Thus the complete equation may be written—

$$NH_3 + H_2O + CO_2 + NaCl \rightleftharpoons NH_4Cl + NaHCO_3.$$

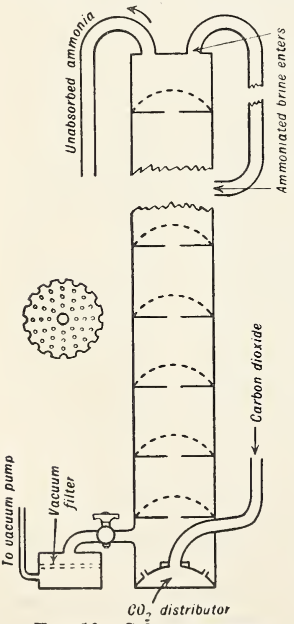


FIG. 19.—Solvay process.

(N.B.—This equation is not so hard as it looks. On the left hand side you simply write down "one of everything".)

Once sodium bicarbonate has been obtained, it has only to be heated in order to turn it into the carbonate—

$$2NaHCO_3 \rightarrow Na_2CO_3 + H_2O + CO_2.$$

We must now consider the main outlines of the actual manufacturing process.

Salt obtained, say, from the Malagash deposits of Nova Scotia, is dissolved in water and saturated with ammonia. It then enters a "Solvay tower", which is about 80 feet high, 6 feet wide, and is furnished at intervals of a yard or so with grids which prevent the brine moving downwards too

fast. Carbon dioxide is pumped in from below and reacts with the ammoniated brine (chiefly at the grids) in accordance with the equation already given.

One or two further points are worth considering. Notice the construction of the grids—very like the rose of a watering can. They are, however, slotted round the circumference (see Fig. 19), and the bicarbonate, formed on the curved surface, slides to this outer rim and finds its way through the slots to the bottom of the tower. It collects there as a sort of white mud, and is pumped off to vacuum filters.

Part of the carbon dioxide required is produced in specially constructed lime-kilns ($CaCO_3 \rightarrow CaO + CO_2$). The remaining part is obtained in the process of turning the sodium bicarbonate into carbonate (equation already given).

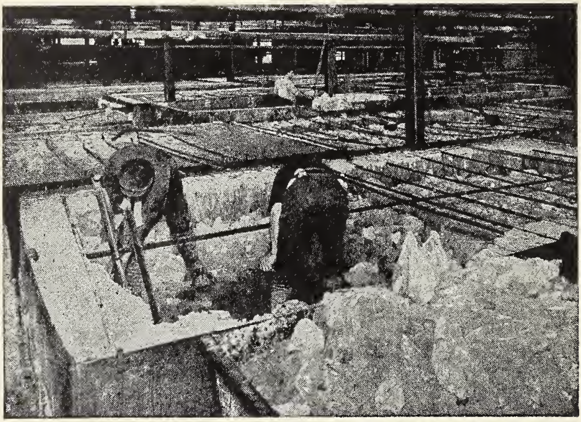
From the ammonium chloride produced in the main process, ammonia is recovered by heating with slaked lime—

$$2NH_4Cl + Ca(OH)_2 \rightarrow CaCl_2 + 2H_2O + 2NH_3.$$

The source of the slaked lime will be sufficiently obvious.

A little ammonia tends to escape unabsorbed at the top of the tower, but this is made to pass through brine which at a later stage will enter the Solvay tower. The actual wastage of ammonia is much less than 1 per cent. In fact, the whole process is a beautiful example of chemical economy, the only waste product being calcium chloride—and in a few years' time that substance will probably be used in connection with the synthetic ammonia process.

The sodium carbonate obtained by heating the bicarbonate consists of a fine white powder, and is known as *soda ash.* On dissolving this in hot water and crystallizing out, *washing soda,* $Na_2CO_3 . 10H_2O$ (often known as *soda crystals*), is obtained (see illustration).



By courtesy of "The Industrial Chemist."
Crystallizing tanks for washing soda crystals.

If exposed to a dry atmosphere, washing soda loses most of its water of crystallization, the glassy crystals becoming covered with a white powder of the composition $Na_2CO_3 . H_2O$. It has already been explained (see p. 26) that such a change is known as efflorescence. On heating, the powder loses its remaining water, but is not otherwise changed. In common with other carbonates, sodium carbonate gives off carbon dioxide when treated with an acid. Its reaction with slaked lime has already been considered on p. 116.

Sodium carbonate finds a use in most homes as a cleansing agent. It is also largely used in the manufacture of glass and in several other industries.

Sodium Bicarbonate (sometimes called "acid sodium carbonate").—One might expect that this would be made *directly* by the Solvay process already described. It is found in practice, however, that a purer product is obtained by turning *all* the sodium bicarbonate first produced

into the carbonate. Any bicarbonate required is then re-formed by dissolving some of the carbonate in water, and passing carbon dioxide through it under slight pressure:—

$$Na_2CO_3 + H_2O + CO_2 \rightarrow 2NaHCO_3.$$

A solution of sodium bicarbonate is slightly alkaline to litmus. It does not injure the skin and can even be squirted into the eye without injurious effect. A wash-bottle of this solution is therefore often kept handy in the laboratory in case anyone should be splashed with acid. With hydrochloric acid for instance, the reaction would be—

$$NaHCO_3 + HCl \rightarrow NaCl + H_2O + CO_2.$$

As already mentioned (page 120) the action of heat on sodium bicarbonate is to turn it into the carbonate. This change takes place quite readily even at the temperature of boiling water.

When sodium bicarbonate is used for baking, the chemical change just mentioned causes carbon dioxide to be produced inside the dough, puffing it out and causing it to be "light" and porous. It has the further advantage (from the confectioner's point of view) of turning it to a light yellow colour as though eggs had been used on a generous scale. Unfortunately the chemical change leaves in the cake a residue of sodium carbonate (*i.e.* washing soda minus its water of crystallization), and if the quantity is considerable, the taste is thoroughly unpleasant.[1]

---

[1] The writer vividly recalls being one of a party which sat down to a farm-house tea after a long country ramble. There was a large dish of rock buns of most inviting "eggy" colour, but scarcely anybody got further than a mouthful or two. The taste of sodium carbonate was very marked.

In Seidlitz powders, " health salts ", etc., the constituents are sodium bicarbonate and (usually) tartaric acid. The latter is a solid, and no action takes place until it is dissolved in water. Hence the injunction to " use a dry spoon ". Baking powder is a somewhat similar mixture, but " cream of tartar " (potassium hydrogen tartrate) is used instead of tartaric acid, and the mixture also contains starch (or flour). The latter prevents atmospheric moisture from gaining access to the other constituents, which would, of course, react with one another if they became damp.

Sodium Sulphate, Na_2SO_4.—This is usually made in the first stage of the old Leblanc process, which you will no doubt have studied, but in western Canada (chiefly in Saskatchewan), there are large natural deposits estimated by the Dominion Department of Mines at 120 million tons, and these are now being worked to a rapidly increasing extent (5,000 tons in 1929, over 31,000 tons in 1930).

The illustration suggests how some of them at any rate are formed. Springs charged with sodium sulphate in solution well up from the ground, the water evaporates and the solid matter remains behind.

Sodium sulphate crystallizes out with ten molecules of water of crystallization, and this apparently trifling circumstance is a definite handicap to the Western Canada deposits in competing with the artificial product. The latter, obtained by the action of sulphuric acid on sodium chloride, is *anhydrous*,—and it is the anhydrous substance which is chiefly required in industry. The natural deposits contain "$10H_2O$", and the getting rid of this water of crystallization is a very definite item in the expense sheet.

Sodium sulphate is used in certain smelting operations and also in the manufacture of wood-pulp and glass. The

refined product is used in medicine under the name of Glauber salt.

By courtesy of Dept. of Mines, Ottawa.

Cone of sodium sulphate forming round spring, Ingebright deposit, Saskatchewan.

Sodium Thiosulphate, $Na_2S_2O_3 . 5H_2O$, is so called because it may be regarded as sodium sulphate, Na_2SO_4, in which one atom of oxygen is replaced by one of sulphur (Gr. *theion*). It may be prepared by boiling a solution of sodium sulphite with flowers of sulphur, as far as possible excluding air (which tends to oxidize the sodium sulphite to sulphate).

In the bleaching industry it is used as an "antichlor", *i.e.*, as a substance for removing excess of chlorine, with which it reacts thus—

$$Na_2S_2O_3 + H_2O + Cl_2 \rightarrow Na_2SO_4 + S + 2HCl.$$

It was also owing to this reaction with chlorine that a solution of sodium thiosulphate was used in gas-masks during the Great War. Under the name "hyposulphite of

soda'' (hypo) this salt is largely used in photography because of its property of dissolving silver bromide, with which it forms a soluble salt—

$$Na_2S_2O_3 + AgBr \rightarrow NaAgS_2O_3 + NaBr.$$

This question is dealt with more fully in connection with compounds of silver (p. 208).

Test for Sodium Compounds.—Practically all sodium compounds are soluble in water, and, therefore, very few "precipitation" methods are available. Sodium compounds are recognized by the fact that they give an intense yellow colour to the bunsen flame. This is seen, for instance, when bending glass tubing, which contains sodium silicate.

Questions (Chapter IX)

1. By what physical properties can we usually distinguish metals from non-metals? In what respects are lead, sodium, and charcoal, exceptions to the general rules?

2. "Metals give rise to basic oxides, non-metals to acid-forming oxides." Illustrate the statement from the cases of zinc and carbon.

3. What is a hydride? Give the name and formula of one hydride of each of the following: oxygen, phosphorus, sulphur, carbon, nitrogen. What can usually be said about an element that forms a hydride?

4. What volume of hydrogen measured at 10° and 75·2 cm. pressure would be obtained by the action of excess of water on 84 gm. of calcium hydride? (Gram-molecule of a gas at N.T.P. occupies 22·4 litres.)

5. "The physical properties of an alloy are by no means the 'average' of those of its constituents". Illustrate as fully as you can.

6. Describe the froth-flotation process, explaining as well as you can the way in which it works.

7. In Ontario, sulphuric acid is often manufactured from the sulphur dioxide produced during the roasting of zinc sulphide (see p. 111). What weight of zinc sulphide would have to be roasted to obtain 100 tons of pure sulphuric acid by this method?

8. What special advantages does Canada possess as a metal-producing country?

Questions (Chapter X)

1. The properties of the elements lithium, sodium, potassium, rubidium, and caesium change with a certain regularity as the atomic weight increases. Illustrate this statement as fully as you can.

2. Describe and explain the change that takes place when a piece of freshly-cut sodium is left for a long time exposed to the air.

3. How do you account for the " caking " of common salt, and for the fact that salt can be obtained which is free from this defect?

4. Briefly state the reactions by which

   (*a*) washing soda can be obtained from common salt,

   (*b*) caustic soda can be obtained from washing soda.

   How would you carry out (*b*) in the laboratory?

5. Mention four gases which would be absorbed by a solution of caustic soda, and give equations for the possible reactions.

6. Of what would the solution in an "oxone" generator (p. 118) consist? Give the equation which represents its formation.

7. What would be the theoretical yield of washing soda from 10 tons of common salt?

8. Calculate the simplest formula of a substance having the following percentage composition:—oxygen, 16·8; sodium, 16·1; carbon, 4·2; water of crystallization, 62·9. What is this substance?

9. Calculate the volume of dry carbon dioxide, measured at 15°C. and 75 cm. pressure, which would be required to convert 30 gm. of caustic soda into (*a*) sodium carbonate, (*b*) sodium bicarbonate. (See note in italics, p. 20.)

CHAPTER XI

POTASSIUM

Occurrence.—Potassium compounds are very widely distributed, *e.g.* as feldspar, $K_2O . Al_2O_3 . 6SiO_2$. By the weathering of this substance potassium carbonate is produced (p. 97), and it is in this way that many soils obtain the potassium compounds without which they cannot be fertile.

Commercially, potassium compounds are obtained chiefly from the Stassfurt deposits in Germany. Here there are beds from 50 to 130 feet in thickness, consisting chiefly of carnallite, $KCl . MgCl_2 . 6H_2O$. Very large deposits of potassium compounds have been recently discovered at Solikamsk in the Urals, and Soviet authorities claim that these are the largest potash deposits in the world.

Extraction.—Potassium was first isolated in 1807 by Sir Humphrey Davy, by the electrolysis of fused caustic potash (KOH). He had been at work on the subject for many months, and when the silvery globules of potassium made their appearance " He could not contain his joy; he literally bounded about the room in ecstatic delight; and some little time was required for him to compose himself sufficiently to continue his experiment."

The method employed at the present time for the extraction of potassium is similar in principle to that employed by Davy. The metal comes into the market in the form of spheres about the size of peas, and is kept under petroleum. It is very soft, and silvery-white when freshly cut. Its chief physical properties have already been given on p. 114, and there also its action on water is discussed.

Potassium forms a number of very important compounds, and we shall now give short accounts of some of them.

Potassium Chlorate.—When chlorine is passed into a *hot* solution of caustic potash, the following reaction takes place—

$$6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O.$$

When the solution is concentrated by evaporation and cooled down, potassium chlorate crystallizes out. This method can be made to give good results in the laboratory, but is no longer used on a manufacturing scale, because five-sixths of the comparatively expensive caustic potash used is turned into potassium chloride, the cheapest of all potassium compounds.

If instead of starting with *potassium* hydroxide we start with the extremely cheap *calcium* hydroxide (slaked lime), we obtain *calcium* chlorate and chloride (try to write the equation with the help of the one just given). If, now, to this solution we add a strong solution of the cheap potassium chloride, we have—

$$Ca(ClO_3)_2 + 2KCl \rightarrow 2KClO_3 + CaCl_2.$$

On cooling, the potassium chlorate crystallizes out (it is not very soluble at low temperatures), leaving the very soluble calcium chloride in solution.

This method completely drove out the older one, but has now been itself to some extent displaced by an electrolytic process. Platinum electrodes are placed close together in a hot solution of potassium chloride, with the result that caustic potash and hydrogen are produced at the cathode and chlorine at the anode (*cf.* electrolysis of sodium chloride, page 45). The chlorine is caused to come into contact with the caustic potash, and reacts with it according to the equation already given ($6KOH + 3Cl_2 \rightarrow 5KCl + KClO_3 + 3H_2O$). Special means are adopted for separating the chlorate, and the re-formed potassium chloride once more undergoes electrolysis.

In our earlier work we have seen that potassium chlorate is used in the laboratory for preparing oxygen. "Chlorate tablets", which people suck when they have a sore throat, also consist of this substance. Potassium chlorate is chiefly used, however, in connection with the manufacture of matches, already discussed on p. 83.

Potassium Nitrate, KNO_3.—For centuries this has been in great demand for the manufacture of gunpowder. Most of it is now made from sodium nitrate (obtained from Chile) and potassium chloride (Strassfurt deposits). On heating a mixture of the two in solution, we have the reversible reaction

$$NaNO_3 + KCl \rightleftarrows NaCl + KNO_3.$$

We cannot make the reaction run to completion by precipitation because all the substances concerned are soluble. However, potassium nitrate at *low* temperatures is much the least soluble of the four salts present, so it can be crystallized out and the reaction proceeds mainly from left to right. You can do the experiment very easily for yourself in the laboratory.

When strongly heated, potassium nitrate decomposes, yielding the nitrite and oxygen,

$$2KNO_3 \rightarrow 2KNO_2 + O_2.$$

Its use in gunpowder depends chiefly on the fact that it rapidly oxidizes carbon to carbon dioxide (*cf*. q. 3 on p. 134).

When heated with sulphuric acid it gives nitric acid—

$$KNO_3 + H_2SO_4 \rightarrow KHSO_4 + HNO_3.$$

Besides its use in gunpowder, potassium nitrate is also employed in pickling meats and in medicine. It is an excellent fertilizer, but too expensive for general use.

Potassium Bromide, KBr, may be made by adding bromine to a warm solution of caustic potash until the

liquid begins to acquire a permanent yellow tinge—

$$6KOH + 3Br_2 \rightarrow 5KBr + KBrO_3 + 3H_2O$$

(*cf.* action of chlorine, p. 129).
The solution is now evaporated to dryness, and heated with a little charcoal to convert the bromate into bromide—

$$2KBrO_3 + 3C \rightarrow 3CO_2 + 2KBr.$$

The chief properties of potassium bromide have already been considered in Chapter V. Make sure that you know how it is acted upon by sulphuric acid (p. 59) and by a mixture of sulphuric acid and manganese dioxide (same page). It is also important to know how a solution of potassium bromide is acted upon by chlorine (p. 58).

Potassium bromide is much used in photography, especially in the preparation of the silver bromide needed for making the sensitive plate or film. We shall deal with this subject in connection with silver bromide (p. 207). It is also employed in medicine.

Potassium Iodide, KI.—This may be prepared by a method similar to that just given for potassium bromide. Its chief properties and uses have already been dealt with in Chapter V, and you should re-read its reactions with (*a*) sulphuric acid, and (*b*) sulphuric acid and manganese dioxide (pp. 61, 59).

Potassium Hydroxide, KOH.—The methods described for the preparation of sodium hydroxide (p. 116) have their parallel in the case of potassium hydroxide, *i.e.* (*a*) electrolysis of a solution of potassium chloride, and (*b*) boiling a solution of potassium carbonate with slaked lime. The electrolysis process is the one chiefly employed on the large scale.

Its properties are so similar to those of sodium hydroxide (p. 116) that it is scarcely necessary to describe them. In the laboratory it is often used to absorb carbon dioxide ($2KOH + CO_2 \rightarrow K_2CO_3 + H_2O$.) For this purpose it has one definite advantage over sodium hydroxide,

for potassium carbonate is easily soluble in a solution of potassium hydroxide. Hence when a solution of potassium hydroxide has been partly turned into carbonate according to the equation just given, the carbonate remains in solution. Sodium carbonate, however, is much less soluble in a solution of sodium hydroxide, and so it tends to crystallize out and choke up the tube by which the carbon dioxide is entering the apparatus.

Like sodium hydroxide, potassium hydroxide is used in the manufacture of soap, but in this case the product is *soft* ("soft soap").

Potassium Carbonate, K_2CO_3.—Every gardener knows that the ash obtained by burning wood or other vegetable matter is a good fertilizer. This is owing to the presence of potassium carbonate. The pure substance was formerly obtained by putting the ash in pots and extracting the soluble carbonate with water, whence the name *potassium* (a sort of imitation Latin derived from *pot-ash*).

We might expect that potassium carbonate would be manufactured by applying the Solvay process (p. 119) to potassium chloride. In this case, however, we should be wrong. *Sodium* bicarbonate easily separates out in the Solvay process because of its rather slight solubility, and the carbonate is then readily obtained by heating the bicarbonate. *Potassium* bicarbonate is much more soluble and therefore does not crystallize out.

Much of the potassium carbonate of commerce is made by first strongly heating potassium chloride with sulphuric acid to turn it into the sulphate.

$$2KCl + H_2SO_4 \rightarrow K_2SO_4 + 2HCl.$$

The sulphate is next heated with a mixture of limestone and fine coal

$$K_2SO_4 + CaCO_3 + 4C \rightarrow K_2CO_3 + CaS + 4CO.$$

The product is known as *black ash*, its colour being due to the presence of coal-dust, etc. The calcium sulphide

present is insoluble, so the potassium carbonate is easily extracted by means of water.

Potassium carbonate crystallizes from solution as $K_2CO_3 . 2H_2O$, while sodium carbonate usually separates as $Na_2CO_3 . 10H_2O$. Generally speaking, however, it resembles the sodium compound in chemical properties. On heating the hydrated compound, the anhydrous salt K_2CO_3 is easily obtained. This is deliquescent, and is sometimes used as a dehydrating agent.

Potassium carbonate is used in the preparation of "hard glass", which usually contains potassium silicate.

Potassium Sulphate, K_2SO_4.—This is present in the mineral kainite, $K_2SO_4 . MgSO_4 . MgCl_2 . 6H_2O$, which is found at Stassfurt. The potassium sulphate is separated by a somewhat complicated process of fractional crystallization. It is used in very large quantities as a fertilizer, and also in the preparation of potash alum, $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$.

Potassium Chloride, KCl.—As already mentioned, this substance (present in the Stassfurt deposits as *carnallite,* $KCl . MgCl_2 . 6H_2O$), is the chief source of the world's supply of potassium compounds. During the Great War, Germany took care that none should leave the country, and other countries had to resort to all sorts of shifts to make up the deficiency. Even so the shortage was very acute, and some potassium compounds rose to twenty and thirty times their normal price.

Potassium chloride is used as a fertilizer, and is the substance from which, directly or indirectly, most other potassium compounds are manufactured.

Test for Potassium Compounds.—Potassium compounds are recognized by the fact that they give a lilac colour to the bunsen flame. Unfortunately, the presence of very small quantities of sodium compounds (often present as impurity) produces a strong *yellow* colour, which quite masks the lilac tint. To get over the difficulty, the flame is viewed through "cobalt glass" (blue). This cuts off

the yellow light but has little effect on the other, and so the potassium compound can be identified.

Questions

N.B.—See note in italics, p. 20.

1. What weight of pure feldspar ($K_2O . Al_2O_3 . 6SiO_2$), supposed to be completely weathered, would give rise to 1 ton of potassium carbonate? (Answer to 2 decimal places.)

2. What volume of oxygen measured at 13°C. and 74 cm. pressure, could be obtained by strongly heating 20 gm. of potassium nitrate?

3. The reaction which accompanies the explosion of gunpowder is believed to be expressed approximately by the equation $4KNO_3 + 2S + 6C \rightarrow 2K_2S + 2N_2 + 6CO_2$. On this basis, what should be the percentage composition of gun-powder?

4. You are required to obtain a jar of *atmospheric* carbon dioxide, and you have access to solid caustic potash and any other chemicals and apparatus you may require. How would you proceed?

5. Do you think the fertilizing power of wood ash would be impaired by exposure to (*a*) dry air, (*b*) rain? Give reasons.

6. From wood ash, limestone, and iodine how could you prepare a specimen of potassium iodide?

7. Make as complete a list as you can of the difficulties that countries would experience when they were cut off from the Stassfurt deposits during the Great War.

CHAPTER XII

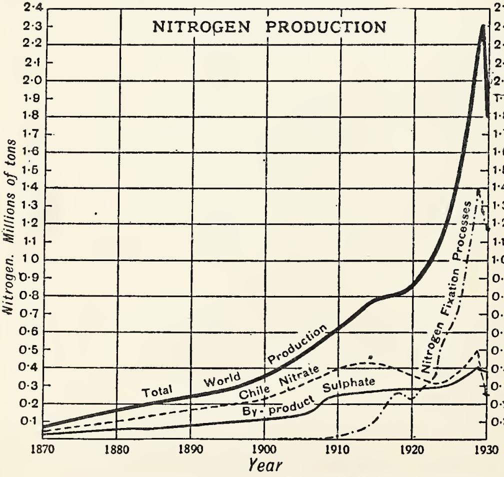
SOME COMMERCIAL FERTILIZERS

Woods, prairie land, etc. in their wild state never require the addition of fertilizers. The native trees and grasses take their necessary food from the soil, but when they die and decay they give back all they have received and so the soil is not impoverished. Animals may live on the vegetation, but from their waste products during life and their bodies when dead, the soil regains all it had lost. We can imagine a simple sort of farm of which the same would be true. But in the modern farm the state of things is entirely different. Large crops are raised and sent away, perhaps for thousands of miles, with the result that the soil is quickly impoverished unless its losses are made good by some form of fertilizer. In practice it is found that the elements which most often require to be replaced are *nitrogen, phosphorus,* and *potassium.* These are by no means the only elements present in an ordinary crop. There is carbon, for instance, present in *all* vegetable products (as we are reminded when vegetable substances are "charred" by partial burning). But the plants obtained this carbon from the carbon dioxide of the air, so the soil has not really lost anything so far as this element is concerned. Again, vegetable matter often contains small quantities of iron compounds, but the amount of these present in the soil is so great as to be practically inexhaustible.

Looking at the three elements mentioned, (nitrogen, phosphorus, and potassium), we might think that the air would supply an abundant quantity of the first. Plants, however, (with a few exceptions) can make no use of the

nitrogen present in the air. They must have nitrogen presented to them in the form of compounds—nitrates, for instance,—and when a soil has lost its supply of nitrogen compounds it ceases to be fertile. This point was mentioned in the Introduction (p. 2), but it is convenient to draw attention to it once again.

There is really a great choice of forms in which nitrogen may be added to the soil. We may add sodium nitrate, for instance, $NaNO_3$, or an ammonium salt such as the sulphate, $(NH_4)_2SO_4$. Farm-yard manure contains various nitrogen compounds including urea, $CO(NH_2)_2$. (Incidentally we may note that farm-yard manure contains compounds of phosphorus and potassium as well as of nitrogen, and is an ideal fertilizer. The trouble is that the supply is hopelessly inadequate.)



By courtesy of "Journal of the Society of Chemical Industry."

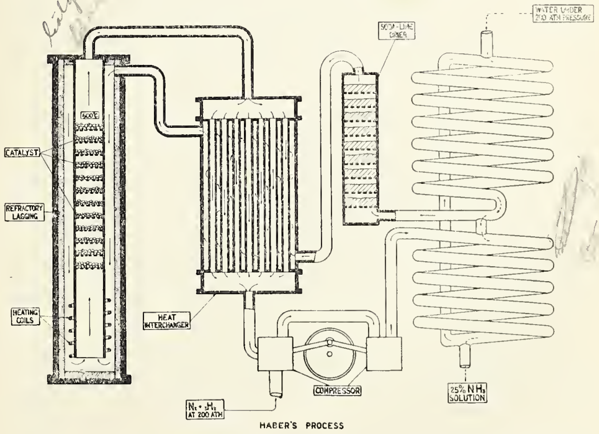
FIG. 20.

Until about 1915, the chief artificial nitrogen fertilizer was sodium nitrate obtained from Chile (Chile saltpetre).

By that time, however, several excellent methods had been discovered by which the nitrogen of the air could be "fixed" (*i.e.* made to combine with other elements), and at the present time these artificial nitrogen products are used to a much greater extent than Chile saltpetre—a point which will be clear from the graph on p. 136.

Of the various "fixation" processes, much the most important is one in which nitrogen is made to combine with hydrogen forming "synthetic ammonia". The processes differ in detail, but the broad principles are the same in each, and may be described somewhat as follows:

A mixture of nitrogen and hydrogen is introduced into a closed circuit at a pressure of about 200 atmospheres. It passes through strong steel spiral tubes in the same direction as a current of water (also under 200 atmospheres pressure), and then, *via* the soda-lime drier and the heat interchanger,



(*By courtesy of Messrs. Baird & Tatlock, London, Eng.*)

Fig. 21—Synthetic ammonia by the Haber process.

down the outer tube of the catalyst bomb,—a very strong chamber made of chrome-tungsten steel. Passing up the inner tube, it is first heated by an electric furnace, and then, at a temperature of about 550°C., passes over trays containing the catalyst, usually consisting of a rare metal known as molybdenum mixed with very pure powdered iron. In contact with the catalyst some 12 per cent. of the nitrogen and hydrogen combine to form ammonia.

The mixture (ammonia *plus* much unchanged nitrogen and hydrogen) now passes once more through the heat interchanger, but in the reverse direction. It then passes through the compressor, where it is reinforced by fresh supplies of nitrogen and hydrogen, and enters the water coils. Here the ammonia is dissolved out, a 25 per cent. solution being formed, and the unchanged nitrogen and hydrogen traverse the circuit once more. Once these gases have been pumped into the apparatus they never leave it except as ammonia.

The "heat exchange" arrangements are worth a passing notice. Ammonia is an *exothermic* compound, *i.e.,* heat is given out when it is formed from its elements. It is evidently desirable that this heat should be handed on to the gases which have still to pass through the furnace, as the heat required from the latter can then be greatly economized. The incoming gases receive this heat as they pass (*a*) through the interchanger and (*b*) down the upper part of the outer tube of the catalyst bomb.

At higher pressures the proportion of nitrogen and hydrogen which combines is greater. In some works pressures up to 1000 atmospheres (say 6½ tons to the square inch) are now employed, and 40 per cent. of the gases can then be made to combine in a single cycle.

The ammonia thus produced is for the most part turned into ammonium sulphate, $(NH_4)_2SO_4$. The SO_4 group may, of course, be obtained from sulphuric acid, (H_2SO_4), but a much cheaper process is now in use, in which "anhydrite" or native calcium sulphate, $CaSO_4$, is employed. This substance is suspended in water in which ammonia has been dissolved, and the suspension is then treated with

carbon dioxide. Calcium carbonate is precipitated, and ammonium sulphate is readily obtained from the solution.

$$CaSO_4 + H_2O + 2NH_3 + CO_2 \rightarrow CaCO_3 + (NH_4)_2SO_4.$$

It is interesting to note that synthetic ammonia is now being made in Canada (at Sandwich, Ontario and at Trail in British Columbia). At Trail the necessary hydrogen is obtained by electrolysis, the cells being capable of producing over three million cubic feet per day. (At present, unfortunately, the oxygen which is produced at the same time has to be wasted.) The pressure employed is between 200 and 300 atmospheres, and the works can turn out some 150 tons of ammonium sulphate per day. The SO_4 group in the ammonium sulphate is obtained not from anhydrite, but from sulphuric acid.

We must next consider the question of phosphorus as a fertilizer. Fertile soils contain phosphates, usually calcium phosphate, $Ca_3(PO_4)_2$. This is insoluble and is therefore not available as a plant food, but by the action of carbonic and other acids in the soil and in the root sap, it is gradually turned into the much more soluble " acid phosphate ", *e.g.*

$$Ca_3(PO_4)_2 + 2H_2CO_3 \rightarrow CaH_4(PO_4)_2 + 2CaCO_3.$$

Now it may easily happen that if land has been cropped several times, the amount of available phosphate (*i.e.* soluble acid phosphate) becomes insufficient for the needs of the plant. The obvious course is to add a supply. To make it, calcium phosphate is ground up and treated with sulphuric acid—

$$Ca_3(PO_4)_2 + 2H_2SO_4 \rightarrow CaH_4(PO_4)_2 + 2CaSO_4.$$

The reaction is carried out in a horizontal cast-iron cylinder with revolving blades inside. As these move round, the mixture is pushed out in a semi-fluid state and drops into pits known as dens, where the reaction is gradually completed. After a day or two the *superphosphate* as it is called becomes solid and is removed. It is crushed and finally dried by means of hot air.

The calcium phosphate used in this process is usually "phosphate rock" mined in the U.S.A. Canada has considerable supplies of apatite, $3Ca_3(PO_4)_2 . CaF_2$, but it occurs in "pockets" and is comparatively expensive to mine, while the U.S.A. deposits are in broad layers and can be mined cheaply. Hence, though superphosphate is made in Canada, it is mainly from imported phosphate rock. Superphosphate is sometimes made from bones, which contain a large proportion (about 58 per cent.) of calcium phosphate.

Another form in which phosphates may be supplied to the soil is *basic slag*. "Pig iron" usually contains a small amount of phosphorus, and unless this is removed, steel made from it is of very inferior quality. On p. 184 it will be explained how the phosphorus can be completely converted into a mixture of calcium and magnesium phosphates known as *basic slag,* a substance which finds a ready sale as a fertilizer.

Finally, we should notice that the manufacture of *ammonium phosphate* at Trail, B. C., is a rapidly developing industry. Synthetic ammonia is made as already described, and phosphoric acid is obtained by the action of sulphuric acid on phosphate rock.

$$Ca_3(PO_4)_2 + 3H_2SO_4 \rightarrow 3CaSO_4 + 2H_3PO_4.$$

The phosphoric acid is then treated with ammonia so as to make monammonium phosphate, $NH_4 . H_2PO_4$.

$$NH_3 + H_3PO_4 \rightarrow NH_4 . H_2PO_4.$$

Ammonium phosphate acts quickly because it is readily soluble. Further, it contains combined nitrogen as well as phosphorus and so forms a two-in-one fertilizer.

While nitrogen and phosphorus fertilizers are nowadays, for the most part, artificially prepared, potassium compounds are applied to the ground chiefly in naturally occurring minerals such as *sylvine* (KCl), or occasionally as wood-ash which, as we saw in the last chapter, contains a large quantity of potassium carbonate. Potassium com-

pounds suitable for agriculture have not yet been found in Canada. Some of the salt deposits at Malagash in Nova Scotia contain potassium chloride, but the percentage is too low for profitable extraction.

Obviously, the question of fertilizers is of very first importance to Canada. A great part of her natural wealth consists of her fertile soil, and she must restore to it in the form of nitrogen, phosphates, and potash what she is taking from it in crops. Some day, no doubt, she will produce these fertilizers entirely within her own borders,[1]—as she can already do so far as nitrogen is concerned. With regard to phosphates, several hopeful investigations are in progress, having as their object the utilization of Canadian apatite. The solution of the potash problem seems more remote, but is well within the range of possibility. Supplies of potassium salts may be found, or a method may be evolved for preparing potash from feldspar, of which abundant supplies are available. Research in this direction is already in progress.

Questions

1. Wheat straw contains silica. Why does a farmer not consider it necessary to add silica to his soil?

2. "The works can turn out some 150 tons of ammonium sulphate per day" (p. 139). What weight of (a) ammonia, (*b*) sulphuric acid, would be required for this? What weight of nitrogen is "fixed" in the 150 tons?

3. Assuming that at a synthetic ammonia works, 3,000,000 cubic feet of hydrogen are produced in one day by electrolysis, and used, (*a*) what volume of oxygen would be simultaneously produced, (*b*) what volume of air would have to be treated to produce sufficient nitrogen to combine with the hydrogen, if nitrogen constitutes four-fifths of the air by volume?

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[1] For the year ended June 1931, 19,200 tons of fertilizers were imported as compared with 49,100 tons for the preceding twelve months. These figures are very significant, for consumption during 1931 was practically normal, the difference being made up by supplies manufactured at home.

4. Calculate the percentage of phosphorus in (*a*) "superphosphate", regarded as a mixture of $CaH_4(PO_4)_2$ (one molecule) and $CaSO_4 . 2H_2O$ (two molecules), (*b*) apatite, $3Ca_3(PO_4)_2 . CaF_2$.

5. Basic slag has a composition expressed by the formula $Ca_3(PO_4)_2 . CaO$. Say whether you think the substance is well named, giving reasons.

6. Basic slag is an excellent fertilizer, and so is ammonium sulphate; but farmers say they should not be put on the land at the same time. Why not?

7. It is said that "superphosphate of lime" should not be kept mixed with Chile saltpetre (sodium nitrate). Why not? *Hint.* The $CaH_4(PO_4)_2$ present in superphosphate may be regarded as $Ca_3(PO_4)_2 + 4H_3PO_4$ ($\rightarrow 3CaH_4(PO_4)_2$).

CHAPTER XIII

CALCIUM, STRONTIUM, BARIUM

CALCIUM (atomic weight 40), strontium (88), and barium (137) are the most important members of Group II, family A. All are soft, silvery-white metals of low density (calcium 1·55, strontium 2·54, barium 3·75). All are divalent. Calcium soon tarnishes on exposure to air, and barium oxidizes with such vigour as to be spontaneously inflammable. Strontium, as we might expect, occupies an intermediate potition. All react vigorously with water, forming the hydroxide and liberating hydrogen, *e.g.* $Ca + 2H_2O = Ca(OH)_2 + H_2$. Calcium carbonate is decomposed if kept for some time at a dull-red heat ($CaCO_3 = CaO + CO_2$). Strontium carbonate requires white heat, and barium carbonate still higher temperatures.

In most cases the strontium compounds have a solubility lying between those of the corresponding compounds of calcium and barium. Thus, in the order Ca, Sr, Ba, the hydroxides increase in solubility while the sulphates decrease, barium sulphate, indeed, being a highly insoluble substance.

All these elements fall into the same group in qualitative analysis, and all give characteristic flame tests. Compounds of calcium, for instance, give a brick-red colour.

Calcium

Occurrence.—Calcium is found in nature chiefly as the carbonate, $CaCO_3$. This was originally formed on the sea bottom as chalk (from the remains of tiny marine organisms), the chalk often giving rise by physical change to limestone and marble.

Another very interesting form af calcium carbonate is *calcite* or *Iceland spar.* This consists of transparent rhombic crystals which show the peculiarity known as "double refraction", so that a mark on paper is seen double when viewed through this substance. Its name is due to the fact that it was first found in Iceland, and the best specimens are still obtained in that country from a small quarry which has been worked for nearly 300 years. Crystals as much as a yard across have been taken from it. Iceland spar is used in the construction of certain optical instruments.

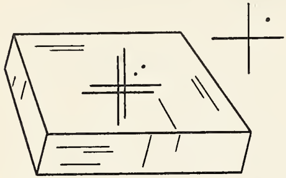


FIG. 22.—Crystal of calcite, showing double refraction.

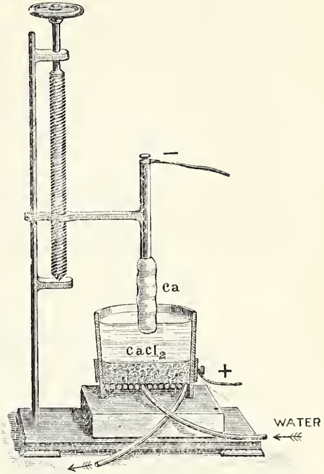
Canada has very large supplies of calcium carbonate. Thus, limestone forms a great part of the front ranges of the Rocky Mountains, giving Alberta unlimited supplies, —used, for instance, in the cement industry. Manitoba limestone is highly esteemed for building, and British Columbia has large supplies of marble. In 1929 the production of limestone in Canada was over 8¼ million tons.

Calcium sulphate also occurs largely in nature, usually in the form of the hydrate, $CaSO_4 . 2H_2O$, known as *gypsum.* Most of the gypsum in Canada is obtained in Nova Scotia, where more than a million tons were produced in 1929. In places there are entire cliffs as much as 150 feet high composed of it. The largest gypsum mine in the world is situated at Caledonia in Ontario.

Extraction.—Calcium is obtained by the electrolysis of fused calcium chloride, a salt which is obtained as a by-product in a number of industries. The cathode consists of an iron rod which at first touches the surface. As the calcium is deposited the rod is gradually screwed up to prevent the metal from being melted by the fused chloride.

Thus a rod of calcium is obtained looking something like a huge cabbage stalk, 10 inches or so in thickness. It is prevented from oxidation by a deposit of calcium chloride which covers it.

Heated calcium combines with all the gases of the atmosphere except argon (and the other very rare inert gases — kryton, xenon, etc.). It has, therefore, sometimes been used for obtaining very high vacua, and also in the preparation of argon.



(*From Partington's "Inorganic Chemistry," by courtesy of MacMillan & Co., Limited.*)

FIG. 23.—Calcium by electrolysis.

Calcium Oxide, CaO, known also as lime or quicklime, is prepared by heating limestone in kilns. In the laboratory it is easily made by heating chalk for about half an hour in a muffle furnace.

$$CaCO_3 \rightarrow CaO + CO_2.$$

On adding water to quicklime much heat is evolved, calcium hydroxide ("slaked lime") being produced—

$$CaO + H_2O \rightarrow Ca(OH)_2.$$

Calcium Hydroxide, $Ca(OH)_2$, is only slightly soluble in water (about 1 part in 600 at ordinary temperatures). The solution is known as lime-water, and is alkaline to litmus. The reaction of calcium hydroxide with carbon dioxide will be familiar.

The milky liquid obtained by shaking up calcium hydroxide with less water than will dissolve it is known as

milk of lime. In other words, milk of lime is a *suspension* of slaked lime in water (strictly speaking, in lime-water).

When heated to dull redness, slaked lime is reconverted into quicklime— $Ca(OH)_2 \rightarrow CaO + H_2O$.

Mortar is made by mixing slaked lime with about three times its weight of sand. "Setting" is due to loss of water by evaporation. This is followed by the much slower process of "hardening", which consists of the gradual change of calcium hydroxide into carbonate, by the action of atmospheric carbon dioxide—

$$Ca(OH)_2 + CO_2 \rightarrow CaCO_3 + H_2O.$$

The water produced at the same time accounts for the fact that a new house often continues to be damp for some months after being built. Sometimes this liberated moisture condenses and trickles down the walls, especially in basements. The mortar is then said to "sweat".

The sand helps to keep the mixture open to atmospheric carbon dioxide, and it prevents excessive shrinkage as the mortar sets and hardens.

The gardener, also, has his uses for slaked lime. He uses it to correct "sourness" in soil, and to keep down slugs and other pests. He finds also that it has a curious effect on clay soil, making it far more workable (*cf.* bottom of p. 98).

Calcium Carbonate, $CaCO_3$.—We have already seen that this substance occurs very widely in nature. By the combined action of water and carbon dioxide (from the air) it is turned into calcium bicarbonate—

$$CaCO_3 + H_2O + CO_2 \rightarrow Ca(HCO_3)_2.$$

Now, calcium bicarbonate is considerably soluble in water, and the result is that limestone hills often contain immense caves and underground channels where the original limestone has been removed.

Naturally, the water in a limestone district will contain calcium bicarbonate in solution. On boiling it, the *reverse* of the change represented by the last equation takes place,

and the calcium carbonate settles to the bottom of the kettle. In time quite a thick crust will accumulate, often coloured brownish by the presence of iron compounds. Tc prevent such a deposit being formed, people sometimes keep a marble in the kettle. This rolls about, and the deposit is unable to stick.

Calcium carbonate is sometimes described as one of the three main pillars of the chemical industry, the other two being coal and common salt. To give only a few examples of its importance, it is used in the manufacture of soda, calcium carbide, glass and bleaching powder, and in the smelting of iron.

Hardness of Water.—Water is often met with which does not readily give a lather with soap. It is then said to be *hard*. When hard water is evaporated to dryness there is always a residue consisting of some calcium[1] salt, usually the carbonate or sulphate. Now soap is the sodium salt of a fatty acid known as stearic acid, *i.e.* soap is sodium stearate.[2] Hence, when hard water containing, say, calcium sulphate is brought into contact with soap solution, a double decomposition takes place:—

$$\begin{matrix}\text{Sodium} & & \text{Calcium} & & \text{Sodium} & & \text{Calcium} \\ & + & & \rightarrow & & + & \\ \text{stearate} & & \text{sulphate} & & \text{sulphate} & & \text{stearate.}\end{matrix}$$

Calcium stearate is insoluble and forms a white precipitate.

You can see it floating about on the surface after you have been washing your hands in hard water.

It is clear that after a time all the calcium salt originally dissolved in the water will have been precipitated as calcium stearate. From that moment the soap will play its ordinary part in producing a lather.

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[1] In some districts a magnesium salt, or there may be both. In what follows, what is said about calcium also applies roughly to magnesium.

[2] Sodium oleate and sodium palmitate are usually present as well. They have an action very similar to that of the stearate.

Hard water, then, brings about waste of soap,[1] converting it into useless calcium stearate. We must, therefore, consider two questions—

(1) How does water become hard?

(2) How can it be softened?

The answer to the first question is that the water must have flowed over land containing calcium compounds. Much the commonest one is calcium carbonate, and we have just seen that by the action of water and carbon dioxide this is turned into calcium bicarbonate which passes into solution. We have also seen that when such water is boiled the calcium salt is thrown out of solution and the water which remains is, therefore, soft.

Hardness which can be removed by boiling, i.e. *hardness due to the presence of calcium bicarbonate in solution, is said to be* ***temporary.***

Temporary hardness is sometimes removed by *Clark's process,* usually applied on the large scale, *e.g.* to the entire water supply of a town. By careful analysis, the amount of calcium bicarbonate in solution is ascertained, and the exact amount of milk of lime is added to precipitate all the calcium in accordance with the equation[2]—

$$Ca(HCO_3)_2 + Ca(OH)_2 = 2CaCO_3 + 2H_2O.$$

If too much milk of lime is added, the water will still be hard—harder than before perhaps. The reason is, of course, that we still have a calcium compound in solution, this time calcium hydroxide.

So much for temporary hardness. If the hardness is due to the presence of some calcium compound other than the bicarbonate—calcium sulphate, for instance—boiling will make no difference.

---

[1] It has been calculated that in London alone the value of the soap wasted in this way is more than $1,000,000 a year.

[2] It has been shown that bacteria present in the water are also carried down with the fine precipitate of calcium carbonate. Thus the water is not only softened but, if previously infected, is made safe for drinking.

Hardness which cannot be removed by boiling is said to be ***permanent.***

Permanent hardness may be removed by the addition of sodium carbonate, washing soda ($Na_2CO_3 . 10H_2O$) being usually employed. This causes the calcium to be precipitated as carbonate [1]—

$$CaSO_4 + Na_2CO_3 \rightarrow CaCO_3 + Na_2SO_4.$$

A modern method of softening water is known as the *Permutit process.* The ordinary house supply of hard water is made to pass through a cylinder containing "permutit," and soft water is drawn off. Let us see how it works.

Permutit, which looks like a coarse sand, is a complex substance which we may describe as sodium alumino-silicate. We will represent it as $Na\overline{P}$. If hard water (containing, say, calcium sulphate) flows over this, we get—

$$2Na\overline{P} + CaSO_4 \rightarrow Na_2SO_4 + Ca\overline{P}_2.$$

Thus, calcium is removed from the water, being left behind in the cylinder as calcium alumino-silicate. After a while the substance ceases to act properly because so much of the sodium compound has been turned into the calcium compound. To restore it, a solution of common salt is poured in and left overnight. We get—

$$Ca\overline{P}_2 + 2NaCl \rightarrow CaCl_2 + 2Na\overline{P}.$$

Thus the sodium alumino-silicate is re-formed, and the process of water-softening can be continued.

Calcium Sulphate.—We have already seen that this occurs naturally as *gypsum,* $CaSO_4 . 2H_2O$. *Anhydrite,* $CaSO_4$ is also frequently found. In some countries (but not at present in Canada) anhydrite is being used in the manufacture of ammonium sulphate (p. 138).

Gypsum has long been used in the preparation of *plaster of paris,* $(CaSO_4)_2 . H_2O$ made by heating gypsum to 125°C. and so causing it to lose three-quarters of its water

[1] Hence, in applying Clark's process, it is usual now to add the calculated quantity of sodium carbonate as well as milk of lime.

(*By courtesy Ontario Dept. of Mines.*)
Gypsum on the Cheepash River in Northern Ontario.

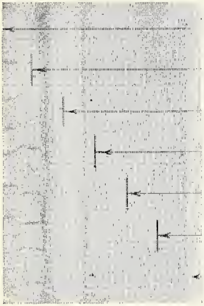
of crystallization. When plaster of paris is mixed with water, heat is evolved and gypsum is re-formed—

$$(CaSO_4)_2 . H_2O + 3H_2O \rightarrow 2(CaSO_4 . 2H_2O).$$

The chemical change is accompanied by " setting ", apparently because gypsum is less soluble than plaster of paris. Let us see how this works out. Suppose a little of the plaster of paris dissolves in the added water. It is now converted into gypsum, which being less soluble crystallizes out. The process is repeated with successive quantities of plaster of paris until the whole of it has crystallized as gypsum. The final result is: (*a*) the added water, if suitable in amount, is all used up—*i.e.* the substance becomes *dry*; and (*b*) the tiny crystals, produced in a confined space, interlock with one another and form a compact mass.

When plaster of paris sets it expands a little. This causes it to press right up to the boundaries of any cavity in which it may be placed, *i.e.* to take a sharp impression. Hence, this substance is often used in making models; a dentist may employ it in obtaining an exact impression of a patient's mouth.

Gypsum products such as tiles, blocks, wallboards, etc. are being used to an increasing extent in building, and their manufacture is developing into an important Canadian industry. They have the very useful property (among others) of helping to prevent the spread of fire from one room to another, or from one building to another. This point is illustrated in Fig 24, representing a gypsum tile



By courtesy of Editorial Services, Ltd.

Fig. 24.—Gypsum as a heat insulator.

six inches thick. One surface was exposed to a temperature of 1200°C,—*i.e.* 100 degrees or so above the melting point of copper. After three hours the temperature at the middle of the block was still below the boiling point of water. Try to explain the result for yourself, keeping in mind (i) that gypsum tiles are porous, and (ii) that in the process of dehydrating gypsum (*i.e.* in driving out its water of crystallization), heat is used up.

Gypsum has many other uses. It is often employed as a plaster for walls and ceilings, while the familiar school "chalk" usually consists of the same substance.

Calcium Carbide, CaC_2, is made by strongly heating a mixture of quicklime and coke in a closed electric furnace —$CaO + 3C \rightarrow CaC_2 + CO$. The substance is familiar because of its use in the preparation of acetylene, often used in bicycle lamps, etc.

$$CaC_2 + 2H_2O \rightarrow Ca(OH)_2 + C_2H_2.$$

When nitrogen is passed over calcium carbide at a temperature of 1100°C., a mixture of calcium cyanamide and graphite is produced ($CaC_2 + N_2 \rightarrow CaCN_2 + C$).

The dark grey mixture is known commercially as *cyanamide* or *nitrolim,* and is sometimes used as a fertilizer, the moisture in the soil causing the slow liberation of ammonia—

$$CaCN_2 + 3H_2O \rightarrow CaCO_3 + 2NH_3.$$

Evidently, by the use of calcium carbide we have another means of "fixing" atmospheric nitrogen.

It is interesting to notice that the cyanamide plant at Niagara Falls, Ont., has the largest capacity of any in the world, and a few years ago was producing more than 100,000 tons a year. It is now producing much less. The tendency is, in fact, for all other fixation processes to give place to some form of the Haber process described on p. 137.

Calcium Chloride, $CaCl_2$, may easily be obtained by dissolving calcium carbonate in hydrochloric acid, as in the preparation of carbon dioxide, and then evaporating the residue. Commercially, it is obtained in large quantities as a by-product in various processes, notably the Solvay process for the manufacture of soda (p. 119). In fact, the man (or boy) who could find a good use for the by-product calcium chloride would probably make his fortune.

The anhydrous salt readily absorbs moisture, forming the hexa-hydrate, $CaCl_2 . 6H_2O$, and so is often used in the laboratory as a drying agent. The hexa-hydrate itself is very deliquescent, and a solution of it is sometimes used in summer to water the streets. You can no doubt think out for yourself how this would help to keep the road moist longer than would ordinary water.

Calcium Oxalate, CaC_2O_4, is produced when ammonium oxalate is added to a calcium salt in neutral or alkaline solution, *e.g.*—

$$CaCl_2 + (NH_4)_2C_2O_4 \rightarrow 2NH_4Cl + CaC_2O_4.$$

Calcium oxalate is so highly insoluble in water that the reaction provides us with a very delicate test for a calcium salt. **Bleaching powder** and **calcium phosphate** are other important compounds. The latter has already been considered on p. 77, and bleaching powder will have been studied in connection with chlorine.

Strontium and Barium

Compounds of strontium and barium are for the most part not so important as those of calcium, but one or two points may be added to those mentioned at the beginning of the chapter.

Barium Sulphate, $BaSO_4$, occurs native as *heavy spar* or *barite.* It is found in many parts of Canada, but the only deposit being worked at present is in Cape Breton Island.

Barium sulphate is used chiefly in the paint and rubber industries, and as a source of other barium compounds (chloride, etc.). As a constituent of (white) paint it has the advantage of retaining its colour even after prolonged exposure. When added to rubber it is found to increase the resiliency of the latter, and to improve its wearing qualities. It is extremely insoluble in water.

Barium Chloride, $BaCl_2 . 2H_2O$, is prepared by heating barite with calcium chloride and coal, at a temperature of 900°C.,—

$$BaSO_4 + 4C + CaCl_2 \rightarrow BaCl_2 + CaS + 4CO.$$

The barium chloride is extracted with hot water and crystallized out.

It is used in the laboratory chiefly in testing for a sulphate, with which it forms a white precipitate insoluble in hydrochloric acid, *e.g.*—

$$Na_2SO_4 + BaCl_2 \rightarrow 2NaCl + BaSO_4.$$

The test is a very delicate one owing to the great insolubility of barium sulphate.

Questions

N.B.—See note in italics, p. 20.

1. Express in tabular form those properties of calcium, strontium, and barium (and their compounds) which indicate that the elements belong to the same family.

2. Sketch an arrangement of apparatus by which, making use of calcium, you might expect to obtain argon from the air, adding just sufficient written description to make your method quite clear.

3. You are asked to find the percentage of calcium carbonate in a mixture of that substance and calcium oxide. How would you set to work?

   Hint. When calcium carbonate is strongly heated for half an hour, it loses 44 % of its weight due to escape of carbon dioxide.

4. A limewater bottle in the laboratory sometimes has a chalky appearance. How is this caused, and how might it have been prevented? How would you clean the bottle?

5. From the fact that in Canada, gypsum is often found in large quantities on the surface, what conclusion would you draw with regard to its solubility?

6. What weight of water would be driven off during the calcination of 1 ton of gypsum?

7. What volume of acetylene, measured at 10°C. and 76 cm. pressure, would be produced by adding excess of water to 4 oz. of calcium carbide? (1 oz. = 28·38 gm.)

8. 1 million cubic feet of nitrogen are absorbed by calcium carbide, and by treatment with steam the cynamide so produced is made to give off all its nitrogen in the form of ammonia. What would be the volume of this ammonia, measured at the same temperature and pressure as the original nitrogen?

9. When pure barium chloride is dissolved in water, the solution obtained is often a little cloudy. Why?

CHAPTER XIV

THE MAGNESIUM-ZINC FAMILY

Magnesium, zinc, cadmium, and mercury make up family B of Group II in the Periodic Table (p. 68). A few of their properties may conveniently be tabulated.

Element	Atomic Weight	Density	Melting Point	Boiling Point
Magnesium	24·3	1·74	651°C.	1120°C.
Zinc	65·4	7·14	419°C.	930°C.
Cadmium	112·4	8·65	320°C.	778°C.
Mercury	200·6	13·60	—39°C.	357°C.

As the atomic weight increases, the elements become less electro-positive (p. 50). This statement sums up a great deal in their chemical behaviour. Thus, each metal will displace a lower one from a solution of one of its salts, *e.g.* zinc will displace mercury from mercuric chloride. Again, magnesium is so strongly electro-positive that it cannot be prepared by reducing its oxide with carbon or hydrogen, while mercury is so feebly electro-positive that its oxide is easily decomposed by heat.

The metals all have a valency of two, but mercury also forms compounds in which the valency is one.

Magnesium

Occurrence.—Magnesium being highly electro-positive is, of course, never found free, but its compounds are widely

distributed. They include *magnesite,* $MgCO_3$; *dolomite,* $MgCO_3 . CaCO_3$; and *carnallite,* $KCl . MgCl_2 . 6H_2O$ (the last being found at Stassfurt). Canada has considerable supplies both of magnesite (chiefly in Quebec) and of dolomite.

Magnesium seems to be an essential constituent of the chlorophyll of plants.

Properties.—In the laboratory, magnesium is usually met with in the form of thin ribbon. It is very bright but gradually tarnishes, and it burns with a flame of dazzling brilliance, whence its use in flashlight photography, etc. Its action on water will have been considered earlier in the course. It dissolves very readily in dilute acids, giving hydrogen.

Magnesium is a constituent of some useful alloys, usually with aluminium. *Magnalium* and *duralumin* are well-known examples.

Magnesium Carbonates.—The normal carbonate occurring native as *magnesite* has already been mentioned. If to a solution of a magnesium salt (*i.e.* the sulphate), we add one of sodium carbonate, a ***basic salt*** (*i.e. a compound of the normal salt with the corresponding oxide or hydroxide* is always precipitated. In this case, the composition of the basic salt varies according to the conditions of precipitation,so we must express it by the general formula

$$xMgCO_3 . yMg(OH)_2 . zH_2O.$$

If the basic carbonate is suspended in water and a stream of carbon dioxide is passed through, the carbonate goes into solution as bicarbonate, $Mg(HCO_3)_2$. This is very similar to what happens in the case of calcium carbonate. A solution of magnesium bicarbonate is sold under the name of *fluid magnesia.*

Magnesium Sulphate is well-known as *Epsom salt* ($MgSO_4 . 7H_2O$), so called because it was formerly obtained from a mineral spring near Epsom in England. It is usually prepared by treating dolomite or magnesite with sulphuric acid, but is sometimes obtained from the waters

of springs, lakes, etc. (See illustration. The "Epsomite" is in this case practically pure Epsom salt).

Epsomite from a lake near Basque, B. C.

Besides its use as a purgative, magnesium sulphate is employed as a dressing for cotton goods.

Magnesium Silicates.—Magnesium forms a number of silicates of very complex formulae, but as explained in the chapter on silica they may usually be regarded as compounds of magnesium oxide, silica, and water in varying proportions. *Serpentine*, for instance, $H_4Mg_3Si_2O_9$, may be written as $(MgO)_3 . 2SiO_2 . 2H_2O$. Other magnesium silicates are *meerschaum, talc,* and *asbestos.*

They are of great commercial importance. Meerschaum is used for articles such as pipe-bowls. Talc (often called soapstone) when very finely ground gives us "French chalk", and is also the base of toilet powders, etc. In the massive form it is used for making sinks, table-tops, etc.

Asbestos mining is an industry of great importance to Canada. The name asbestos is usually given to a magnesium-calcium silicate having the formula $(MgO)_2 . CaO . 4SiO_2$, but Canadian asbestos is really a fibrous variety of serpentine with the formula already given. It is mined in Quebec, and occurs in narrow veins varying from one-eighth to as much as two or three inches in width. It has a slight green colour with a silky

By courtesy of the Canadian Asbestos Co.

Specimen of crude asbestos (about one-quarter actual size).

appearance, and is made up of fibres which can be separated and woven like cotton or silk. Its fire-resisting properties were known to the ancients, who are said to have woven it into shrouds to cover their dead, so that when a body was cremated its ashes would not be mingled with those of the funeral pyre.

Asbestos is resistant not only to the action of fire but also to that of most acids. Further, it is an excellent non-conductor of heat, sound, and electricity. These properties cause it to have a large and ever-increasing number of uses. It is used for packing joints in steam and electrical machinery; for theatre curtains; for furnace linings; for brake-linings of motor cars; for filtering acids; for making roof shingles and tiles. Mixed with sodium silicate it makes an excellent fireproof cement,—but this list might be extended almost indefinitely.

In 1929, over 6 million tons of asbestos-bearing rock were

By courtesy of the Canadian Asbestos Co.
An asbestos mine (Thetford).

mined, yielding some 300,000 tons of asbestos selling for about $13,000,000. Canada, in fact, supplies about 75% of the world's requirements in asbestos.

Zinc

Occurrence.—Zinc is found chiefly as *zinc blende*, ZnS; another important ore is *calamine*, $ZnCO_3$.

Extraction.—We shall give a brief account of the method in use at Trail in British Columbia.

The ore is first roasted, zinc oxide being formed—

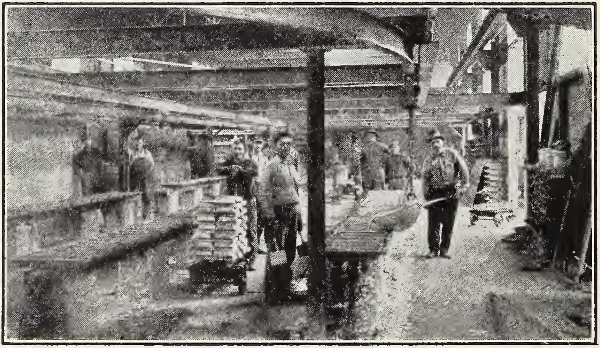
$$2ZnS + 3O_2 \rightarrow 2ZnO + 2SO_2.$$

A portion of the sulphur dioxide is at once converted into sulphuric acid by the contact process.

The zinc oxide produced by the roasting process is now dissolved in the sulphuric acid, a solution of zinc sulphate being obtained—

$$ZnO + H_2SO_4 \rightarrow ZnSO_4 + H_2O.$$

Lastly, the zinc sulphate solution is submitted to electrolysis, zinc of a very high degree of purity (99·95 per cent.) being obtained. The necessary electric current is derived from water-power, of which there is a plentiful



By courtesy of the Consolidated Mining and Smelting Co.
Zinc Melting Room, Trail, B. C.

supply in the neighbourhood. The " cathode zinc " is finally melted up in 100-ton reverbatories, and then hand-ladled into moulds as shown in the illustration.

This method is also in use in several other parts of the world where conditions (cheap water-power, for instance) are suitable.

Properties and Uses.—Zinc is a bluish-grey metal melting at 418° and boiling at 1040°. When quite pure it is insoluble in sulphuric acid, but " commercial zinc " dissolves readily enough. There is little doubt that in the

presence of impurities an electrical action is set up (*cf.* the solution of zinc in a voltaic cell on closed circuit), but the full explanation belongs to Physics rather than to Chemistry. The impurity usually present is *lead,* some of this metal (as sulphide) occurring along with the original zinc blende. Similarly, *galena* (lead sulphide) usually contains zinc sulphide as an impurity (p. 213).

Zinc is often used in the laboratory in the preparation of hydrogen. When making hydrogen by this method, you have probably noticed, after the zinc has dissolved, a lot of black specks floating about in the dilute acid. These specks are the lead of which we have spoken.

Of late years the black specks have been less noticeable—and the zinc has been more difficult to dissolve. The reason in both cases is that purer zinc is being put on the market. In case of difficulty it may be necessary to add a few drops of copper sulphate solution. Zinc acts upon this, liberating copper ($Zn + CuSO_4 \rightarrow ZnSO_4 + Cu$), and the copper then acts, probably, in pretty much the same way as the lead would have done.

Zinc is largely used for "galvanizing" iron, so as to protect it from rusting. Sheet iron, after being thoroughly cleaned, is dipped into a bath of molten zinc. A thin coating of the latter metal clings to it, and as it solidifies it gives the curious crystalline effect that you have seen on new pails, etc.

Much zinc is also used in the manufacture of *brass* (an alloy of zinc and copper).

Zinc Oxide may be prepared by any of the usual methods. It is used in the preparation of a white paint known as "zinc white", and if required for this purpose it is made by burning zinc shavings in the air, when it is formed as a bulky white powder which used to be called "philosopher's wool". Zinc white has not nearly the "body" or covering power that "white lead" possesses, but it has one great advantage. Both zinc oxide and white lead are gradually turned into the corresponding sulphides on exposure to the air of towns (because such air contains small

quantities of hydrogen sulphide). Now zinc sulphide is white, like the original oxide, while lead sulphide is *black*. Hence a white lead paint soon darkens in colour. The darkening of an old oil-painting is due to the same cause. A paint containing zinc oxide would evidently undergo no change of colour.

Zinc oxide may be recognized by its curious property of turning yellow when heated. It regains its white colour on cooling.

Zinc oxide is also the essential constituent of " zinc ointment ".

Zinc Sulphide.—As already mentioned, this is one of the chief ores of zinc. *Lithopone* is a very useful white paint consisting of a mixture of zinc sulphide and barium sulphate. It is prepared by mixing solutions of barium sulphide and zinc sulphate—

$$BaS + ZnSO_4 \rightarrow BaSO_4 + ZnS.$$

Zinc Chloride, $ZnCl_2$ is an extremely soluble, diliquescent salt, usually marketed in the form of fused sticks. It is a powerful germicide and is, therefore, much used in the preservation of timber. It is also employed in surgery as a caustic, and in soldering as a flux.

Zinc Sulphate.—You will have come across this substance while preparing hydrogen from zinc and dilute sulphuric acid. The contents of the flask may be filtered, when the sulphate ($ZnSO_4 . 7H_2O$) readily crystallizes out. It is sometimes known as *white vitriol.* When strongly heated, it is decomposed into zinc oxide and sulphur trioxide—

$$ZnSO_4 \rightarrow ZnO + SO_3.$$

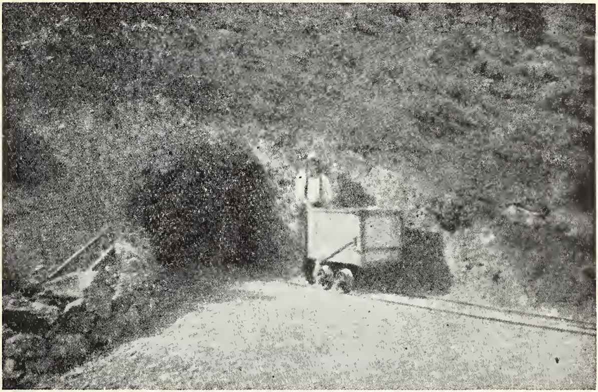
Its use in the preparation of lithopone has already been mentioned. A very dilute solution (1 in 800) is sometimes employed as an eye lotion.

Mercury

Occurrence.—Mercury occurs in nature chiefly as the sulphide, HgS, known as *cinnabar,* a red or black mineral

found in various parts of the world, but chiefly in Spain and Italy. The Almaden mine in Spain (which is still producing) has been worked more or less continuously since B.C. 415.

Small quantities of cinnabar have been located at several points in Canada, the chief deposits being near Kamloops, in British Columbia.



By courtesy of the Canadian National Railways.

Cinnabar Mine, Copper Creek, near Kamloops, B. C.

Properties and Uses.—On account of its high density (13·6) mercury is used in the manufacture of barometers. Its high boiling-point (357°C.) and low freezing-point (—39°C.), together with its regularity of expansion on heating, make it a very suitable liquid for use in thermometers.

It is chiefly useful, however, on account of its power of forming alloys, or **amalgams**, with other metals. Thus, one process for the extraction of gold consists in allowing this metal to come into contact with mercury. A gold amalgam is obtained, and when this is distilled, the mercury passes

over and can be used again, while the gold remains behind.

The zinc plates used in a voltaic cell are brushed over with mercury. This forms a coating of zinc amalgam on the surface, and prevents the zinc from being dissolved except when the circuit is actually closed.

Copper amalgam was formerly much used in dentistry in filling cavities in teeth.

Tin amalgam is used in the backing of mirrors.

Sodium amalgam is sometimes used in the laboratory as a reducing agent. In presence of water, hydrogen is liberated exactly as in the case of sodium itself, but the action is much more gentle.

Mercury, however, does not readily amalgamate with iron, and so the mercury of commerce is marketed in screw-stoppered, iron bottles, each containing 76 pounds.

Mercuric Oxide, HgO.—This substance will already have been considered in connection with oxygen. It is of historical importance because it was by heating it with a burning glass that Priestley obtained oxygen in 1774. The fact that it is so readily decomposed by heat, is connected with the low position of mercury in the electrochemical series (p. 51).

Mercuric Sulphide, HgS.—As already noted, this occurs in nature as cinnabar. In qualitative analysis we meet with it as a black precipitate in Group II. It is easily distinguished from copper sulphide (also black) by the fact that it is insoluble in boiling dilute nitric acid, while copper sulphide is soluble (giving a blue solution of copper nitrate).

In its red form mercuric sulphide provides us with the pigment *vermilion.*

Mercurous Chloride, Hg_2Cl_2.—Note the termination *-ous.* Mercury forms two compounds with chlorine, Hg_2Cl_2 and $HgCl_2$, and the one containing the smaller proportion of chlorine is known as mercur*ous* chloride, the other one as mercur*ic* chloride. Similarly, we have mercurous oxide. Hg_2O, and mercuric oxide, HgO; mercurous sulphate, Hg_2SO_4, and mercuric sulphate, $HgSO_4$, etc.

Mercurous chloride is the white precipitate met with in Group I of qualitative analysis—a fact which should remind us that it is insoluble in water (and in dilute hydrochloric acid). Under the name of calomel it is used in medicine as a purgative.

The usual method of preparation is to heat a mixture of mercuric chloride and mercury in an iron pot, when mercurous chloride sublimes on the lid and can be scraped off ($HgCl_2 + Hg \rightarrow Hg_2Cl_2$). The product is thoroughly boiled with water to extract the soluble (and extremely poisonous) mercuric chloride, some of which always sublimes unchanged.

The reason for writing the formula as Hg_2Cl_2 rather than HgCl will best be understood by working out question 10 at the end of this chapter.

Mercuric Chloride, $HgCl_2$, ("corrosive sublimate"), is made commercially by heating an intimate mixture of mercuric sulphate and common salt ($HgSO_4 + 2NaCl \rightarrow Na_2SO_4 + HgCl_2$). Flasks with specially long necks are used, and the mercuric chloride condenses in the upper part of these.

Like other soluble compounds of mercury, it is very poisonous, but is employed in minute quantities in medicine. The surgeon uses a very dilute solution of it (1 part in 1000 parts of water) for sterilizing his hands and his instruments—it kills bacteria.

Several other compounds of mercury are used in medicine. They were introduced by Paracelsus, a physician who taught that the object of Chemistry was not to turn base metals into gold but to prepare medicines. No doubt he did his best, but most of us would have hesitated to take pills and medicine from a doctor who was making the first early experiments with compounds of mercury.

Questions

1. Mercury has been known from ancient times, magnesium only from the beginning of the 19th. century. How do you account for this?

2. Magnesium has good claims to be placed in the calcium rather than in the zinc family. Find as many points of resemblance (with calcium) as you can.

3. On p. 51 it is shown that certain chemical properties of elements are related to their position in the electro-chemical series. Consider how far this relationship holds goods for magnesium, zinc, and mercury.

4. "Fluid magnesia" is spoilt if the bottle is not kept well corked. Why?

5. Can you suggest why asbestos will not burn?

6. In 1932 at Tadanac, B. C., 800 tons of zinc sulphide was being roasted daily, and one-third of the sulphur dioxide produced was being turned into sulphuric acid. What would be the output of sulphuric acid?

7. 6 gm. of crystallized zinc sulphate was gently heated in a crucible until the weight was constant. This constant weight was 3·37 gm. Calculate the number of molecules of water of crystallization.

8. The painted walls of a chemistry laboratory sometimes go dark after only a few months. Why? Suggest a practical test which you could apply to the paint which it is proposed to use for such a laboratory.

9. The two chlorides of mercury contain, respectively, 15·07 per cent. and 26·21 per cent. of chlorine. Show that these numbers are in accordance with the Law of Multiple Proportions.

10. Mercurous chloride contains 84·9 per cent. of mercury, and when carefully dried it has a vapour density of 235·5. Find (*a*) its empirical formula, (*b*) its molecular formula.

11. Compare the compounds mercurous chloride and mercuric chloride under the following headings:—(*a*) Formula, (*b*) Usual method of preparation, (*c*) Solubility, (*d*) Volatility, (*e*) Reaction with stannous chloride (see p. 213).

CHAPTER XV

ALUMINIUM

Occurrence and Extraction.—With the exception of oxygen and silicon, aluminium is the most abundant of all the elements present in the earth's crust, and it is certainly the most abundant metal. As we saw in Chapter VIII, ordinary clay consists largely of aluminium silicate. The ore from which the metal is extracted, however, is a hydrated oxide known as *bauxite,* $Al_2O_3 . 2H_2O$. This ore has not so far been found in Canada. The extraction of aluminium is, however, largely a question of cheap electric power, and the result is that Canada actually possesses the largest aluminium plant in the world,—the Arvida works in the Saguenay district. The necessary power is obtained from a part of the Saguenay river known as the Chute à Caron, capable of supplying 800,000 h.p. The bauxite is imported from British Guiana.

In extracting aluminium, the bauxite is first carefully purified from iron, because the aluminium finally obtained is found to be of very inferior quality if iron is present. Without going into details, we may say that the separation from iron depends on the fact that aluminium oxide (or "alumina") is soluble in a solution of caustic soda[1], while the iron compounds are insoluble.

No doubt alumina *could* be electrolyzed by first melting it and then introducing electrodes, etc., but as it only melts at 2050°C., *i.e.* well above the melting-point of wrought iron, such a process would be quite impracticable.

In Greenland, however,—and nowhere else so far—there is found a mineral, *cryolite,* a double fluoride of sodium

[1] Forming sodium aluminate, $NaAlO_2$. *Cf.* equation on page 171 (last line on the page).

and aluminium with the formula $AlF_3 . 3NaF$ (or Na_3AlF_6). Now a mixture of cryolite and alumina melts at about 900°C. Here we have quite a manageable temperature, and the electrolysis proceeds just as though only the alumina were undergoing change; so that except to make up for a little wastage there is no need to replenish the cryolite. In practice, a certain amount of calcium fluoride is also added.

The electrolysis is carried out in an iron vessel lined with gas-carbon, the vessel being connected with the negative terminal of a dynamo, *i.e.* the vessel itself is the

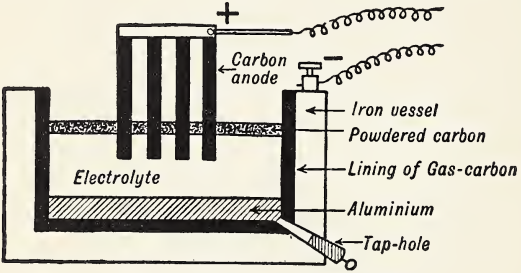


FIG. 25.—Extraction of aluminium.

cathode. The anode consists of a number of rods of carbon. The voltage required is low (5 or 6 volts), but a current of about 10,000 amperes is required for each cell. The passage of such a powerful current keeps the mixture in a state of fusion.

There is one difficulty which, so far, nobody has succeeded in overcoming. As the carbon anode is all the time in contact with oxygen at a high temperature, it is burnt away very rapidly and has constantly to be replaced. In fact, for every ton of metal produced, about a ton of anodes is burnt away. If it were not for the expense of providing such a stock of anodes, aluminium would be even cheaper than it is.

Properties and Uses.—Aluminium has an enormous number of uses. Cookery utensils of all sorts are made

of it, partly because it is scarcely attacked by air or water. As a matter of fact, in contact with air, a very thin film of oxide is deposited on it. This oxide adheres very firmly and protects the metal underneath from further change—it is just as though the surface had been painted or varnished. For the same reason, aluminium paint forms an excellent covering for iron work of all kinds.

A rather serious objection to the use of aluminium was that it could not be *soldered.* This difficulty has now been overcome, but a special solder has to be used (aluminium, 2·25; phosphor-tin, 0·75; zinc, 17; tin, 80).

Aluminium is being used to an increasing extent for the transmission of electric current. An aluminium wire has certainly a higher resistance than a copper wire of equal thickness. By using thicker wire, however, we can reduce the resistance, and an aluminium wire of 1·64 sq. mm. cross-section would have the same resistance as a copper wire of 1 sq. mm. But the relative density of aluminium is only 2·58 compared with 8·91 for copper, and the result is that the thicker wire just mentioned would actually weigh less than half as much as the thinner copper wire. In short, *weight for weight* the resistance of an aluminium wire is less than half that of a copper one.

At high temperatures aluminium shows a great affinity for oxygen. Thus, if a mixture of ferric oxide and aluminium powder is ignited, the aluminium takes oxygen from the ferric oxide and reduces it to iron—

$$2Al + Fe_2O_3 \rightarrow Al_2O_3 + 2Fe.$$

The mixture is conveniently ignited by lighting a piece of

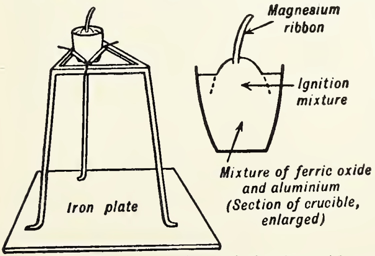


FIG. 26.—Reduction of ferric oxide by aluminium.

magnesium ribbon which terminates in a little pile of barium peroxide mixed with magnesium filings as shown in Fig. 26. The experiment should be carried out in a fire-clay crucible. The heat produced is so intense that the iron is actually melted.

This reaction has received a number of useful applications. A piece of apparatus has been devised in which the molten iron can be run out of the bottom of the crucible on any given spot—a crack in a steel propeller, for instance. The metal on each side of the crack melts, runs together, hardens, and the crack is thus sealed up. Joints between rails may be sealed up in the same way. The process has been patented and is known as the " Thermit process ".

If instead of mixing the aluminium with *ferric* oxide, we mix it with *chromium oxide,* metallic chromium is produced ($2Al + Cr_2O_3 \rightarrow Al_2O_3 + 2Cr$). In a similar way a number of the less common metals have been very conveniently obtained.

At high temperatures aluminium also combines with *nitrogen* forming aluminium nitride, AlN. For this reason manufacturers of steel and some other metals often add a minute proportion of aluminium to the molten product. This combines with any bubbles of atmospheric nitrogen that may be present—the metal itself will probably have combined with the oxygen,—and so prevents the formation of " blow-holes ", which would be a source of weakness.

Aluminium forms a number of very useful alloys. *Magnalium,* for instance (magnesium + aluminium), is lighter even than aluminium, and, unlike that metal, can be worked easily in a lathe. Among other purposes it is used for making the beams of chemical balances.

Duralumin (aluminium 94·4 parts + small quantities of magnesium, copper, and manganese) can be hardened and tempered. It is used in airship construction. Aluminium also forms a number of valuable alloys with copper. They are known as aluminium bronzes.

When we remember the number of new uses which are

constantly being found for aluminium and its alloys, it is not surprising to find that the output of the metal is advancing by leaps and bounds. From practically nothing at all in 1890, it had risen to 7000 tons in 1900, to 64,000 tons in 1913, and 200,000 tons in 1931!

Aluminium Oxide.—The hydrated oxide, bauxite, has already been mentioned. Its chief use, of course, is as a source of aluminium, but some is also used in making bauxite cement ("ciment fondu"). This is prepared by fusing together bauxite and quicklime in nearly equal proportions, forming a "clinker" which after being allowed to cool is ground up very finely. The cement thus obtained will resist the action of sea-water, which ordinary cement will not.

The anhydrous oxide alumina, Al_2O_3, occurs native as *corundum.* This may be coloured by the presence of traces of other oxides giving rise to various gems—the ruby, topaz, sapphire, and emerald. A number of these are now made artificially by fusing alumina in the oxy-hydrogen flame and adding the necessary colouring oxide. Thus, by adding chromium oxide, artificial rubies have been produced which can scarcely be distinguished from the natural article.

Corundum is nearly as hard as diamond. An impure variety of it, known as *emery,* is much used in grinding and polishing.

Aluminium Hydroxide, $Al(OH)_3$, is met with as a gelatinous precipitate when ammonium hydroxide is added to an aluminium salt in the course of analysis, *e.g.*

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 2Al(OH)_3 + 3(NH_4)_2SO_4.$$

It dissolves readily in sodium hydroxide forming a solution of sodium aluminate—

$$Al(OH)_3 + NaOH \rightarrow NaAlO_2 + 2H_2O.$$

This equation does not convey very much perhaps. Let us write it in a slightly altered form,—" doubled all through ", and afterwards with the hydroxides represented as compounds of oxides and water. We get

$$2Al(OH)_3 + 2NaOH \rightarrow 2NaAlO_2 + 4H_2O.$$
$$\text{or } Al_2O_3 . 3H_2O + Na_2O . H_2O \rightarrow Na_2O . Al_2O_3 + 4H_2O.$$

It will be clear from this that sodium aluminate may be regarded as a compound of a basic oxide (Na_2O) with an acidic oxide (Al_2O_3), just as sodium sulphate, Na_2SO_4, may be regarded as a compound of Na_2O (basic) with SO_3 (acidic).

But aluminium hydroxide also dissolves readily in acids —in sulphuric acid, for instance, forming the sulphate,

$$2Al(OH)_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 6H_2O,$$

or $Al_2O_3 . 3H_2O + 3(SO_3 . H_2O) \rightarrow Al_2O_3 . 3SO_3 + 6H_2O$. Now, SO_3 represents a well-marked *acidic* oxide, so that alminium oxide must in this case be acting as a *basic* oxide.

A study of aluminium hydroxide, therefore, leads to the conclusion that *aluminium oxide can function either as a basic or as an acidic oxide according to circumstances.* It is basic in the presence of a well-marked acidic oxide, and acidic in the presence of a well-marked basic one. It is, in fact, *amphoteric* (*cf.* arsenious oxide, p. 85).

The fact is that aluminium hydroxide, $Al(OH)_3$, can ionize either thus:— $Al(OH)_3 \rightleftarrows Al^{+++} + 3OH^-$ (i)
or thus:— $Al(OH)_3 \rightleftarrows AlO_2^- + H^+ + H_2O$ (ii)
If we add an *acid*, say sulphuric acid, the hydrogen ion introduced removes hydroxide ion (forming water). Thus in (i) equilibrium is displaced to the right, while in (ii) it is dsplaced to the left (because ''collisions'' between AlO_2^- and H^+ obviously take place with increased frequency). The final result is that practically the only ions present are Al^{+++} and SO_4^{--} (from sulphuric acid), *i.e.* we have a solution of aluminium sulphate.

Similar reasoning shows that if instead of adding acid we introduce hydroxide ion (OH^-) by adding sodium hydroxide, we shall obtain a solution of sodium aluminate.

Elements near the left of the Periodic Table form strongly basic oxides; elements on the right form acidic ones. It is not very surprising then that some elements near the centre should form oxides partaking of both characters.

Aluminium Sulphate, $Al_2(SO_4)_3$, is made on a large scale by dissolving bauxite in dilute sulphuric acid—

$$Al_2O_3 + 3H_2SO_4 \rightarrow Al_2(SO_4)_3 + 3H_2O.$$

The product often contains ferric sulphate (owing to the presence of ferric oxide as an impurity in the bauxite). It is then known as *alumino-ferric.*

Aluminium sulphate (or, more often, alumino-ferric) is largely used for purifying water which is contaminated with sewage. The first action is the production of aluminium hydroxide by hydrolysis (aluminium sulphate being the salt of a weak base + strong acid; (*cf.* p. 50).

$$Al_2(SO_4)_3 + 6H_2O \rightleftarrows 2Al(OH)_3 + 3H_2SO_4.$$

The sulphuric acid is removed as fast as it is produced, either by reacting with the calcium bicarbonate present (p. 147) or in the case of very soft water with slaked lime which is specially added. (Write the equations.) Thus, the reaction represented by the above equation goes completely from left to right.

Now when first produced, the hydroxide is in what is known as the colloidal condition *i.e.* the particles are smaller than even the finest of those of a substance in suspension, and the total surface presented is, therefore, very large. The particles of sewage are *adsorbed* (not absorbed), *i.e.* they cling to the surface of the particles of colloidal aluminium hydroxide. The latter soon run together or coagulate, and then settle to the bottom, carrying the sewage particles with them. Most of the injurious bacteria are carried down at the same time.

It may seem strange that just because the aluminium hydroxide is in the colloidal condition (and therefore presenting a very large surface) it should have the power of *holding* small particles with which it comes into contact. It is really a consequence of the special forces which come into play at a surface. " Surface tension " is a familiar example.

While on the subject, we may notice that the cleansing action of soap has a very similar explanation, the colloidal particles of soap adsorbing the particles of " dirt ". Unlike aluminium hydroxide, however, the colloidal soap particles do not coagulate, and so the dirt adsorbed by them remains in suspension.

Aluminium Acetate, $Al(C_2H_3O_2)_3$, is used for waterproofing delicate cotton goods. The latter are steeped in

a solution of the acetate and then steamed. Hydrolysis takes place and aluminium hydroxide is deposited within the fibres of the material, which thus becomes non-absorbent—

$$Al(C_2H_3O_2)_3 + 3H_2O \rightarrow 3H \, . \, C_2H_3O_2 + Al(OH)_3.$$

(N.B.—Acetic acid has the formula $H \, . \, C_2H_3O_2$, one hydrogen atom only being replaceable by metal. Thus, sodium acetate would be $NaC_2H_3O_2$, lead acetate, $Pb(C_2H_3O_2)_2$, and aluminium acetate, $Al(C_2H_3O_2)_3$.)

Dyeing.—A stain on linen or cotton, say from the juice of stewed fruit, will often " come out in the wash "; but most housewives are gloomily aware of the fact that the stain usually persists on a silk or woollen article, especially on the former. The material is " dyed ".

There seem to be two factors at work causing the silk (or wool) to attach itself so firmly to the colouring matter.

(1) The proteins of which the silk is composed are chemically rather reactive, and form insoluble compounds with the coloured matter. Linen or cotton consists of cellulose (Chapter XXIII) and this is much less reactive.

(2) Silk is a colloid, and this adsorbs the coloured material much as (colloidal) aluminium hydroxide was seen to adsorb impurities in water.

Cotton is also a colloid, but apparently the adsorbing action is not sufficiently strong to hold the dye. We can, however, greatly reinforce this action by impregnating the cotton fibres with aluminium hydroxide. When this is done and the fabric is afterwards treated with a dye, the latter is firmly held. A substance added to a fabric in order to enable it to take a dye is known as a **mordant.** For basic dyes a mordant often used is tannic acid. It is a colloid, and so acts as already described, and further, being an acid, it combines chemically with the basic dye. For acid or neutral dyes aluminium hydroxide may be used. It must be deposited within the fibres, which consist of extremely fine tubes. This is done by first soaking the fabric in aluminium acetate and then steaming as described

above; or the fabric may be treated first with a solution of aluminium sulphate and then with ammonia—

$$Al_2(SO_4)_3 + 6NH_4OH \rightarrow 3(NH_4)_2SO_4 + 2Al(OH)_3.$$

Alum.—Ordinary " alum " or " potash alum " has the formula $K_2SO_4 . Al_2(SO_4)_3 . 24H_2O$, but we must notice that this is only one of a large number of alums. Thus, ammonium alum is $(NH_4)_2SO_4 . Al_2(SO_4)_3 . 24H_2O$, and chrome alum is $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$. We may define an alum, in fact, as a compound having the formula $R'_2SO_4 . R'''_2(SO_4)_3 . 24H_2O$, where R' and R''' are univalent and trivalent metals respectively.

To return to potash alum. It is prepared by adding potassium sulphate to aluminium sulphate, and crystallizing out. The solution is definitely acid to litmus, owing to partial hydrolysis of the aluminium sulphate (the equation has already been given on p. 173). In fact, a solution of alum when mixed with sodium carbonate will cause carbon dioxide to be evolved, and on this fact depends the action of certain fire-extinguishers. By inverting the extinguisher, a solution of aluminium sulphate is brought into contact with a solution of sodium bicarbonate mixed with a special foaming ingredient such as saponine, liquorice, etc. The result is the production of a good foam which contains, in each bubble, a quantity of carbon dioxide. Such an appliance is very useful for extinguishing oil fires, water, in this case, being of little use because the blazing oil floats on its surface.

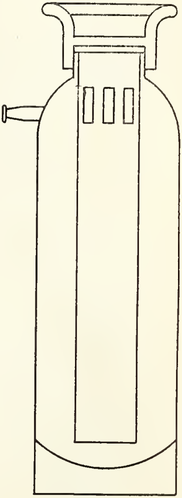


FIG. 27.—Fire extinguisher.

Alum has other uses. It possesses the power of coagulating certain colloids, and a barber often puts a little *burnt alum* on a small cut to make the blood (a colloidal solution) coagulate or " clot ". Burnt alum is the substance produced when ordinary alum is heated to 200°C. to make it lose all its water of crystallization.

Then fabrics are sometimes dipped in a solution of alum, and afterwards dried, to render them non-inflammable. Fire easily causes the alum contained in them to melt (the melting point is 92°) and the molten substance then forms a barrier between the fabric and the air.

Questions

1. How much pure bauxite, $Al_2O_3 . 2H_2O$, would be required for the manufacture of 108 tons of aluminium?

2. What *chemical* properties underlie the use of aluminium for (*a*) making saucepans, (*b*) thermit welding? Give some account of the latter process.

3. It is sometimes said that the present Age of Steel may very easily give place to an Age of Aluminium. Set out briefly what seem to you to be the arguments for and against.

4. Explain carefully what is meant by the statement that aluminium forms an amphoteric oxide.

5. It is said that aluminium pans should not be washed with soda. Why not?

6. What do you mean by hydrolysis? Show that this process plays an important part in (*a*) the waterproofing of cotton fabrics (*b*) the purification of water contaminated by sewage.

7. How much alum would have to be heated in order to secure 100 gm. of burnt alum?

8. A compound has a molecular weight of 998, and its percentage composition is as follows:—K, 7·82; Cr, 10·42; SO_4,38·47; H_2O, 43·29. Calculate its formula. What is it?

CHAPTER XVI

THE IRON FAMILY

(Iron, Cobalt, Nickel)

Iron, cobalt, and nickel occur together in Group VIII of the Periodic System. Their atomic numbers (Chapter XXVIII), atomic weights, densities, and melting points all lie close together, as will be seen from the following:—

	Iron	*Cobalt*	*Nickel*
Atomic numbers	26	27	28
Atomic weights	55·8	58·9	58·7
Densities	7·85	8·72	8·9
Melting points (°C.)	1533°	1480°	1452°

All three metals are magnetic. At a red heat all of them oxidize in the air, and all decompose steam at high temperatures. All form oxides of the type RO, R_2O_3, and R_3O_4.

With carbon monoxide they form curious compounds known as carbonyls, $Fe(CO)_4$, $Co(CO)_4$, and $Ni(CO)_4$. The last mentioned compound is made use of in the Mond process for the extraction of nickel (p. 193).

Occurrence.—We may notice at the outset that iron, like most other metals, is seldom found in nature in the free or uncombined condition. It is very easy to see why. Judging by the material thrown out by volcanoes, there is plenty of free sulphur not far below the earth's surface, while, in contact with the surface, there is, of course, the oxygen in the air. Thus, a metal is pretty certain to be turned either into sulphide or oxide, the oxide often becoming a carbonate by combining with atmospheric carbon dioxide. It is evident, then, that apart from quite

special circumstances, the only metals likely to be found free are such as do not readily form either sulphide or oxide. Gold is an example.

Iron is found in nature chiefly as *haematite,* Fe_2O_3, *magnetite,* Fe_3O_4, and *iron pyrites,* FeS_2. Magnetite is so called because specimens of it are sometimes permanently magnetic ("lodestone"). Iron pyrites is largely used as a source of sulphur dioxide in the manufacture of sulphuric acid. It is burnt in special furnaces called pyrites burners, and ferric oxide is left.

Haematite and magnetite — both oxides of iron — are largely used for smelting purposes, and so is the ferric oxide left after the burning of pyrites in the manufacture of sulphuric acid. From this source alone more than 150,000 tons of ferric oxide of high quality, ready for smelting, were being obtained annually up to a few years ago.

The smelting process is very briefly as follows. The charge, consisting of a mixture of iron ore, limestone, and coke, is introduced by means of a cup-and-cone arrangement into the top of a blast-furnace. The latter has the shape indicated in the figure, and may be about 80 ft. high and 20 ft. broad at its broadest part. A blast of air, previously heated, enters the furnace (at about 6 ft. from its base), through pipes called *tuyeres.* There are often six or more of these, all of them branching off from a wider pipe which encircles the furnace. One of the tuyeres is represented near the bottom on the left.

In contact with the hot coke, the oxygen of the air is converted into carbon monoxide ($2C + O_2 \rightarrow 2CO$). (At such a high temperature it is probable that the dioxide is not formed first.) This carbon monoxide reduces the iron ore—

$$Fe_2O_3 + 3CO \rightarrow 3CO_2 + 2Fe.$$

Now pure iron melts at 1530°C.—some 400° higher than the temperature of the furnace even at its hottest part. As it descends the furnace, however, the iron formed as in the

last equation gradually takes up carbon and acquires a much lower melting-point (the melting-point of a substance is usually lowered by the presence of impurity). It, therefore, melts and collects at the bottom of the furnace, from which it is run out from time to time.

Let us now consider the part played by the limestone. At the high temperature of the furnace this soon gives off carbon dioxide, forming calcium oxide—

$$CaCO_3 \rightarrow CaO + CO_2.$$

Iron ore naturally contains a good deal of earthy material mixed with it, and much of this is silica (SiO_2), the oxide of the non-metal silicon. Now, just as calcium oxide readily combines with carbon dioxide, forming calcium carbonate ($CaO + CO_2 \rightarrow CaCO_3$), so it will combine with silicon dioxide, forming calcium silicate ($CaO + SiO_2 = CaSiO_3$).

Thus the calcium carbonate is turned first into oxide and then into silicate. At the temperature reached in the furnace this silicate easily melts, forming slag, which, being much lighter than molten iron, collects on the top of it and is run off from the slag-hole.

If limestone were not used, the furnace would soon be choked up with sand and clay, and would need cleaning out. By turning the sand, etc., into a fusible silicate, the furnace is practically self-cleaning, and when once set going will remain "in blast", as it is called, for years. Further, the molten silicate forms a protecting layer over the iron, and prevents it from being re-oxidized by the action of the hot blast.

The escaping gases contain about 25 per cent. of carbon monoxide. They are led through a special stove called a "Cowper stove", where the carbon monoxide is burnt. The heat thus produced is made to heat the air which is to be used for the blast, for it is found that if hot air is used, less coke is needed in the furnace. It is worth noting that the percentage of carbon monoxide in the escaping gases is so high because the reaction between ferric oxide

and monoxide is reversible. We discussed a number of such cases in Chapter II.

The molten iron is run into moulds made in sand, the product being known as pig iron or cast iron. It contains 3 - 4 per cent. of carbon, together with small quantities of sulphur, silicon, phosphorus, and manganese.

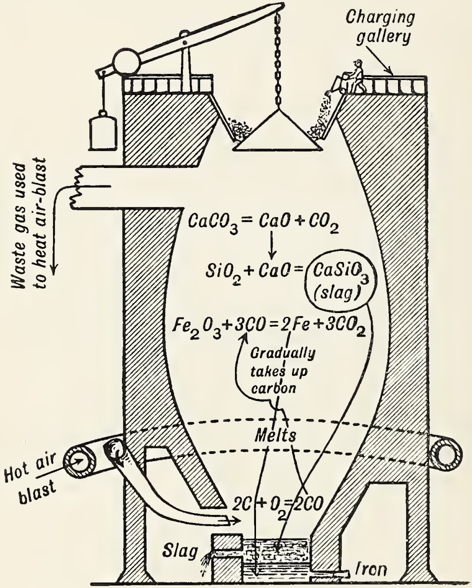
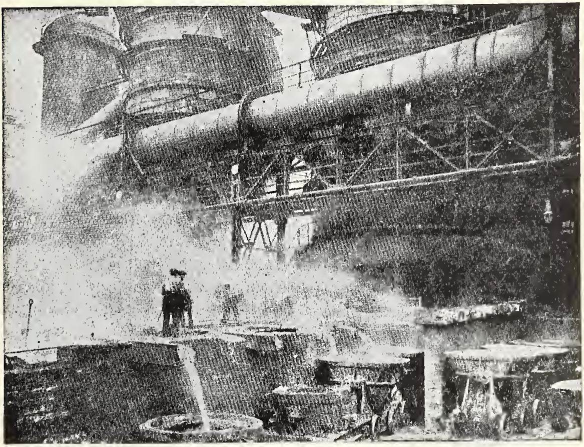


FIG. 28.—Diagram illustrating blast-furnace.

Cast Iron, Wrought Iron, and Steel.—The cast iron just mentioned has a low melting-point (for iron)—about 1100°C.—and has the further property of expanding when it solidifies; hence it is very useful for making castings It is poured into a mould of sand, and on solidifying it pushes its way into every crevice of the mould, thus giving a " sharp " casting.

By a special process the carbon may be almost completely removed from cast iron, the product being known as *wrought iron.* This has a melting-point of about 1500°C. —much higher than that of cast iron. At a red heat, however, it is malleable, *i.e.* it can be beaten out with a hammer, and it is on this property that the blacksmith's work



By courtesy of "The Times".

A Middlesbrough ironworks.

depends. Further, two red-hot pieces may be welded,—beaten together and made to form one piece. Cast iron is brittle and cannot be treated in these ways. Wrought iron is still used for making horse-shoes and the cores of electro-magnets, but for most other purposes it has been superseded by *steel.*

Steel contains up to about $2\frac{1}{4}$ per cent. of carbon, *i.e.* it contains more than wrought iron, but less than cast iron. Like wrought iron, it can be hammered out and welded,

but its most remarkable property is that it can be hardened and tempered. It is hardened by making it red-hot and then suddenly cooling it. It is then extremely brittle, and so hard that small wheels for scratching glass can be made from it. If it is now heated up to a moderate temperature (230° — 330°) and cooled, the metal is much less brittle than before, and is therefore of far more general use. It is said to have been *tempered.* Its exact degree of hardness, etc., will depend on the (second) temperature to which it was heated and on the conditions under which it was cooled (*e.g.* slowly or quickly). Thus, by varying the treatment, we may obtain steel of different properties—some suitable for making razor blades, other for large saws, and so on.

To turn cast iron into steel, we must evidently reduce the carbon content; and, as a slight change in the percentage makes a great difference to the quality of the steel, it is necessary that this percentage should be known with accuracy. The method, therefore, is first to remove *all* the carbon by a process which will be described presently, and then to add the calculated amount of carbon (usually included in a special variety of pig iron known as *spiegeleisen*).

Modern methods of steel manufacture date from 1856, when Henry Bessemer invented a process in which the whole of the carbon (and other impurities) was first burnt away by blowing air through the molten pig iron, spiegeleisen being then added as already mentioned. The old-fashioned steel manufacturers treated Bessemer's process with some contempt at first, but when they found that he could produce better steel than theirs and could afford to sell it at £20 a ton cheaper, they were obliged to take serious notice of it. Soon they were paying Bessemer large sums of money for the right to use his patent,—in fact the inventor made more than a million pounds out of his discovery. Later, he was knighted. He died in 1898 at the age of eighty-five.

The Open-hearth Process.—Of late years the Bessemer process has gradually given place to the *open-hearth,* or *Siemens-Martin* process. Molten pig iron, conveyed straight from the blast-furnace, is run into HH′, the shallow hearth of a furnace. A suitable quantity of good hæmatite is added, and the charge is strongly heated from above by the flames of burning producer-gas.

The oxygen necessary to oxidize away the carbon, sulphur, etc., is not obtained from the air as in the Bessemer process, but is present in the hæmatite (Fe_2O_3), which is itself, of course, reduced to iron in the process. When the

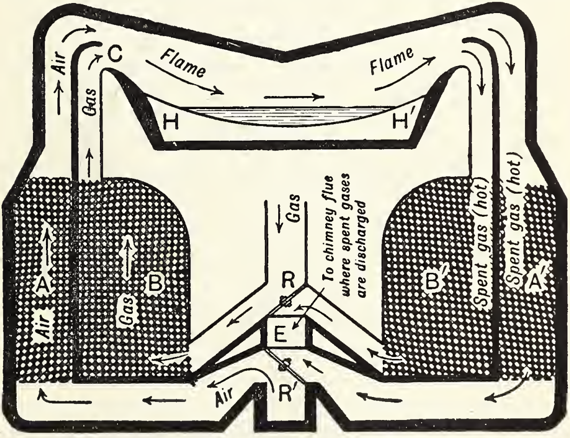


Fig. 29.—Open-hearth process.

carbon, etc., have been removed, spiegeleisen is added and the heating is continued a little longer to ensure thorough mixing. After this, the furnace is tilted (by the action of a hydraulic cylinder), and the steel is poured out.

The open-hearth process takes about as many hours as the Bessemer process takes minutes. This very slowness is in some ways an advantage, however, as it enables the process

to be more accurately controlled, and so an even better quality of steel can be produced.

As an example of heat economy, the general arrangement of a Siemens-Martin furnace is well worth a little notice. Air passes through the chamber A, filled with loosely piled bricks and previously heated to about 1100°C. Similarly, producer-gas passes through the heated chamber B. At C, just on entering the furnace, the gas meets the air, and burns with a great flame which fills the furnace, this flame being so much hotter because the air and gas were preheated. The spent hot gases pass through the brick-filled chambers A′ and B′, heating them as they pass through, and finally reach E, which is connected with the chimney-flue through which they escape into the air. After about half an hour the reversing valves R and R′ are turned through a right-angle. It will be clear from the figure that the supplies of air and gas now go through A′ and B′. which have just been thoroughly heated by the spent gases, and after combustion pass outwards via A and B, which are now heated up in their turn.

Basic Slag.—Bessemer had found that one of the most troublesome impurities to get rid of was phosphorus. However, in 1878, a man named Thomas overcame the difficulty. He lined the vessel in which the steel was manufactured with dolomite (a double carbonate of calcium and magnesium). Now by the action of the air-blast (in the Bessemer process), or by the oxidizing action of the hæmatite (in the Martin process), the phosphorus present is turned into phosphorus pentoxide, an *acidic* oxide, P_2O_5. Calcium carbonate, by loss of carbon dioxide, easily becomes calcium oxide, CaO, a *basic* oxide. The basic and the acidic oxides then combine, forming calcium phosphate, and in a similar way we have magnesium phosphate produced from the magnesium carbonate present.

This mixture of calcium and magnesium phosphates is known as *Thomas's basic slag,* and farmers will pay a good price for it as a fertilizer.

Properties of Steel.—We have already seen that the hardness and brittleness of steel depend largely on the way in which the process of tempering has been carried out. This capacity for taking a temper may be regarded as one of the general properties of steel. Another general property is that it is malleable, though not always at ordinary temperatures. Other properties depend on the composition of the particular steel concerned, and we shall now consider a few of the different varieties.

Different Kinds of Steel.—For simplicity we have so far spoken only of the presence of carbon in steel. For generations, however, it has been known that steel is improved by the presence of manganese, which is present in the spiegeleisen already mentioned.

Of late years, other elements besides carbon and manganese have been introduced, and it has been found possible to make steel having almost any desired properties. Thus *nickel steel* (containing about 3 per cent. of nickel and about 0·25 per cent. of carbon) is extremely hard without being brittle, and is, therefore, used for the armour-plating of battleships—a brittle steel would be shattered if struck by a shell. It is also being used in the automobile industry for parts that are subject to special strain, *e.g.* crank shafts, transmission gears, connecting rods, etc.

Ordinary steel contains, in addition to carbon, a small amount of manganese—0·24 per cent. or so. *Manganese steel,* however, contains a much larger proportion, about 12 per cent. Its properties are somewhat similar to those of nickel steel. It is often used for the jaws of the rock-crushing machinery employed in mining, and during the War was used for making helmets to protect our soldiers against shrapnel. Unlike ordinary steel, it retains its hardness after being heated and cooled, and so is used in making safes. A burglar may heat part of such a safe with his blow-pipe, allow it to cool, and then get to work with his drill, hoping to find that the metal has been softened. In spite of such severe treatment there is not

the least loss of temper—at least not so far as the steel is concerned.

Another way in which safe-manufacturers add to the difficulties of a very trying profession is to make a safe of alternate layers of wrought iron and *chrome steel* (an extremely hard steel containing about 2 per cent. of chromium and from 1 to 2 per cent. of carbon). The hardness of the chrome steel defies the burglar's drill. He then gets to work with his sledge-hammer, only to find that he cannot shatter the wrought iron.

By using larger proportions of chromium—often about 13 per cent.—the familiar *stainless steel* for making cutlery is produced. At first, this steel could not be hardened sufficiently to take a good cutting edge, but this difficulty has now been overcome.

Chrome-tungsten or *high-speed* steel is used for drills. Usually when a drill becomes hot, it also becomes soft and is unable to cut into metal. Hence, the drill has to be worked very gently so that it may not become very hot, and much time is lost. A drill made of chrome-tungsten steel will retain its cutting power even at a dull-red heat.

There are many other kinds of steel, but enough has been said to show that by a suitable admixture of other elements, iron can be made to serve an almost infinite variety of purposes.

Compounds of Iron.—Iron forms two distinct series of compounds:—

(*a*) *Ferrous* compounds in which the iron is divalent, *e.g.* ferrous oxide, FeO; ferrous chloride, $FeCl_2$; ferrous sulphate, $FeSO_4$, etc.;

(*b*) *Ferric* compounds in which it is trivalent, *e.g.* ferric oxide, Fe_2O_3; ferric chloride, $FeCl_3$; ferric sulphate, $Fe_2(SO_4)_3$.

Ferrous salts in the hydrated condition, *i.e.* with water of crystallization) are made by dissolving iron in the appropriate acid. Ferrous sulphate, for instance, is easily made by dissolving a quantity of iron filings in dilute sulphuric acid, filtering to get rid of undissolved iron (or

insoluble impurities) and then leaving to crystallize out ($Fe + H_2SO_4 \rightarrow FeSO_4 + H_2$). The crystals obtained have the composition $FeSO_4 . 7H_2O$.

Ferric salts are easily produced by the oxidation of the corresponding ferrous compounds. Suppose, for instance, we wish to turn ferrous sulphate, $FeSO_4$, into ferric sulphate, $Fe_2(SO_4)_3$. To attain our object we must add an "SO_4" group to $2FeSO_4$. That would give us $Fe_2(SO_4)_3$. The obvious source of the "SO_4" group seems to be sulphuric acid, H_2SO_4, but to liberate this group, the hydrogen must be removed—by oxidation. Thus, we should have—

$$2FeSO_4+H_2SO_4+O \text{ (\textit{from nitric acid})} \rightarrow Fe_2(SO_4)_3+H_2O.$$

Various oxidizing agents may be used, but the best is nitric acid—*best,* because the substances formed by its reduction (chiefly nitric oxide and nitrogen peroxide) are gases, and can, therefore, easily be expelled from the solution.

Anhydrous Ferrous and Ferric Chlorides.—The methods so far described apply only to the preparation of *hydrated* salts. *Anhydrous* iron salts are usually prepared by special methods. Anhydrous ferric chloride, for instance, ($FeCl_3$), is made by passing dry chlorine over strongly heated iron gauze (see Fig. 30). If, instead of chlorine, we use dry hydrogen chloride, anhydrous ferrous chloride, $FeCl_2$, is obtained.

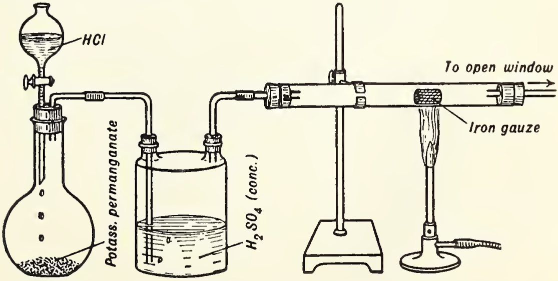


FIG. 30.—Preparation of anhydrous ferric chloride.

Ferrous Salts from Ferric.—We have just seen how to turn ferrous into ferric salts. What about the converse process, ferric to ferrous? Let us consider ferric sulphate, $Fe_2(SO_4)_3$. If we can only get rid of one " SO_4 " group our $Fe_2(SO_4)_3$ will become $2FeSO_4$. It seems as if the most promising method would be to make the "SO_4" group combine with hydrogen. Now, on passing hydrogen through a solution of ferric sulphate, nothing happens. If, however, the hydrogen is generated within the solution, say by adding zinc and dilute sulphuric acid, then reduction soon takes place. The difference is apparently due to the fact that in the second case the hydrogen is *nascent,* while in the first it is not.

$$Fe_2(SO_4)_3 + 2H \text{ (\textit{from} Fe \textit{and} } H_2SO_4) \rightarrow H_2SO_4 + 2FeSO_4.$$

The method as described suffers from one drawback—we have introduced *zinc,* and so our solution of ferrous sulphate would be mixed with zinc sulphate. To avoid this we can use iron filings instead of zinc.

To reduce ferric chloride to ferrous chloride we could use iron and hydrochloric acid—

$$FeCl_3 + H \text{ (\textit{from} Fe \textit{and} HCl)} \rightarrow FeCl_2 + HCl$$

($H =$ an atom of nascent hydrogen), and in fact we may generalize by saying, *To turn a ferric into a ferrous salt, add the corresponding acid and a quantity of iron.*

Distinction between Ferric and Ferrous Salts.—There are many ways of finding whether an iron salt is " ferrous " or " ferric ", but it will suffice to give the following three:—

(1) A solution of a ferrous salt has a watery-green colour, while a solution of a ferric salt is yellow or brown.

(2) If ammonia is added to a solution of a ferrous salt, a green precipitate is obtained. In the case of a ferric salt the precipitate is brown. The precipitates consist of ferrous hydroxide, $Fe(OH)_2$, and ferric hydroxide, $Fe(OH)_3$, respectively, *e.g.*

$$FeCl_2 + 2NH_4OH \rightarrow Fe(OH)_2 + 2NH_4Cl,$$
$$FeCl_3 + 3NH_4OH \rightarrow Fe(OH)_3 + 3NH_4Cl.$$

(3) Ferrous and ferric salts react differently with potassium ferrocyanide and ferricyanide. These reactions will be discussed on p. 191.

Ferrous Sulphate, $FeSO_4 . 7H_2O$ (" green vitriol "), is the most important of the ferrous salts. We already know how it is prepared (p. 186). It is often used in testing for a nitrate.

When strongly heated, green vitriol undergoes changes which are approximately as follows:—

(*a*) Water of crystallization is given off—

$$FeSO_4 . 7H_2O \rightarrow FeSO_4 + 7H_2O.$$

(*b*) The sulphate is decomposed—

$$2FeSO_4 \rightarrow Fe_2O_3 + SO_2 + SO_3.$$

(*b*) Water and sulphur trioxide combine, forming sulphuric acid—

$$H_2O + SO_3 \rightarrow H_2SO_4.$$

Thus, by strongly heating green vitriol under such conditions as are indicated in Fig. 31, it is possible to obtain sulphuric acid. This acid was made from green vitriol many centuries ago by the Arabs, and so received its name of *oil of vitriol—i.e.* the oily liquid obtained by heating green vitriol.

Ferrous sulphate is used in making ink, which consists of a solution of this substance mixed with gum arabic, an organic compound called tannin, and a blue dye. Ferrous tannate is formed in the solution, but this has such a pale colour that the blue dye has to be present to make the writing show. The blue dye, in fact, acts as a temporary ink. On exposure to the air, the ferrous tannate is oxidized to ferric tannate, which has deep black colour.

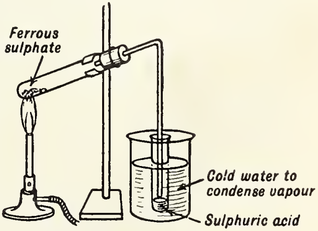


FIG. 31.—Action of heat on ferrous sulphate.

Ferric Oxide, Fe_2O_3, is a red powder which may be prepared by many methods, of which one has just been described. When prepared in this way (*i.e.* by heating green vitriol) the powder is very finely divided, and under the name " jeweller's rouge " is much used by jewellers for polishing silver plate, etc. It is also used in the manufacture of red paint.

We have already seen that ferric oxide occurs in nature as the mineral hæmatite.

Iron rust consists chiefly of the hydrated oxide, $(Fe_2O_3)_2 . 3H_2O$. There is still a good deal of doubt as to the exact conditions necessary for the rusting of iron. Certainly both air and water must be present, but some experimenters say that carbon dioxide is also necessary, and others maintain that at least a slight degree of impurity in the iron is essential. It seems strange that such an " everyday " matter should still be unsettled.

Mixed with other substances, ferric oxide is very widely distributed and has been called " the artist of nature ", because it is so often responsible for imparting colour effects. The red colour of sandstone, for instance, is due to its presence.

Ferroso-Ferric Oxide (= ferrous-ferric oxide), Fe_3O_4, is so called because it may be regarded as $FeO . Fe_2O_3$, *i.e.* a compound of ferrous oxide, FeO, and ferric oxide, Fe_2O_3.

It is this oxide which is produced as a greyish-black substance when steam is passed over heated iron ($3Fe + 4H_2O \rightarrow Fe_3O_4 + 4H_2$). It is also formed when iron is strongly heated in air or oxygen. Thus, "smithy scales," struck by the blacksmith from heated iron, consist of this oxide.

When acted upon by acids it behaves as a sort of mixed base, giving rise to a mixture of ferrous and ferric salts. To obtain the equation we note that FeO would require $2HCl$ (to give $FeCl_2$) and Fe_2O_3 would take $6HCl$(to give $2FeCl_3$). Thus, $FeO . Fe_2O_3$ would need $8HCl$, and we get—

$$Fe_3O_4 + 8HCl \rightarrow FeCl_2 + 2FeCl_3 + 4H_2O.$$

This oxide is found native as magnetite or lodestone (= leading stone), so called because of its magnetic properties. Centuries ago men found that if a piece of the substance were suspended by a cord, its axis always set in a particular direction, and no doubt they often guided themselves over the hills and moorlands with this rude form of compass.

Potassium Ferrocyanide, $K_4Fe(CN)_6 . 3H_2O$, may be prepared by adding potassium cyanide to a solution of ferrous sulphate, until the brown precipitate first formed re-dissolves.

$$FeSO_4 + 6KCN \rightarrow K_2SO_4 + K_4Fe(CN)_6.$$

Potassium ferrocyanide does not behave like an ordinary iron salt, *e.g.* it gives no precipitate on adding ammonia. That is because on dissolving in water it ionizes into $4K^+$ and $Fe(CN)_6^{----}$ while an iron salt would give ions of Fe^{++} (ferrous) or Fe^{+++} (ferric).

With a solution of a ferric salt, potassium ferrocyanide gives a precipitate of ferric ferrocyanide (Prussian blue),—

$$4FeCl_3 + 3K_4Fe(CN)_6 \rightarrow Fe_4(FeC_6N_6)_3 + 12KCl.$$

Potassium Ferricyanide, $K_3Fe(CN)_6$, may be obtained by passing chlorine through a solution of potassium ferrocyanide. On evaporation, it is deposited in the form of dark red crystals (red prussiate of potash),—

$$2K_4Fe(CN)_6 + Cl_2 \rightarrow 2K_3Fe(CN)_6 + 2KCl.$$

With ferrous salts, potassium ferricyanide gives a deep blue precipitate of ferrous ferricyanide,—

$$3FeCl_2 + 2K_3Fe(CN)_6 \rightarrow Fe_3(FeC_6N_6)_2 + 6KCl.$$

Thus, potassium ferrocyanide and ferricyanide are often used in analysis for distinguishing between ferric and ferrous salts.

Blue Prints. Closely connected with the reactions just mentioned is the subject of blue prints, which are prepared as follows. A paper is coated with a mixture of a suitable ferric salt (actually ferric ammonium citrate) and potassium ferricyanide, and dried in the dark. It is then covered over with tracing paper on which has been drawn (in black), the diagram to be printed. On exposure to sunlight, the light causes the ferric salt to be reduced to ferrous salt, but under the black lines this change, of course, does not take place. On washing with water, the usual reaction between a ferrous salt and potassium ferricyanide takes place (see last equation) and the print becomes blue everywhere except along the lines, which are left white. To mark a blue print we can use an " ink " consisting of caustic soda solution, which decolorizes the blue substance.

Cobalt

Cobalt is found chiefly among the silver ores of the Cobalt district of Ontario, the principal ore being *smaltite*, $CoAs_2$,with which there is usually associated some *cobaltite*, CoAsS. We will not enter here into the question of its extraction.

The metal shows great tenacity, and in colour is silver-white with a suggestion of blue. It takes a high polish, is magnetic up to 1100°C. and melts at 1450°C. or thereabouts. Its specific gravity is 8·8 (*cf.* iron 7·8).

Alloys.—*Cobalt steel* (containing 35 per cent.. of cobalt) is being used for the permanent magnets of magnetos. As compared with ordinary steel magnets, they have the advantages that they can be made much smaller, they retain their magnetism much more tenaciously, and have little tendency to become de-magnetized.

Stellite is an alloy of chromium, tungsten, and cobalt. Its hardness and resistance to corrosion make it very suitable for a variety of purposes, including the manufacture of surgical instruments.

Cobalt Chloride, $CoCl_2 . 6H_2O$, may be obtained as dark red deliquescent crystals by dissolving the metal in hydrochloric acid and concentrating the solution. On gently heating, it gives $CoCl_2 . H_2O$ or the anhydrous salt $CoCl_2$, both of which are blue in colour. Hence, a solution of cobalt chloride is sometimes used as " invisible ink ". The trace left by the pink solution is practically invisible, but becomes blue on warming. On cooling and exposure to moist air the colour once more disappears.

Cobaltous Oxide, CoO, is the most important of several oxides of cobalt. It is used for making blue glass, blue patterns on china, etc.

Nickel

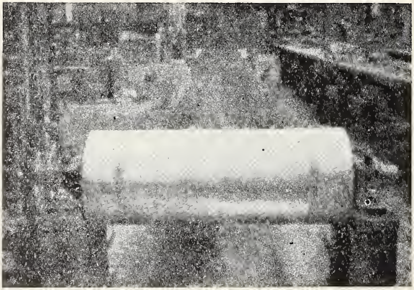
Much the greater part of the world's supplies of nickel are derived from the Sudbury district of Ontario, where the ores consist of a mixture of sulphides of copper, nickel, and iron. After roasting and smelting, a *matte* containing nickel, copper, sulphur, and a little iron is obtained. This is again roasted, and then leached with sulphuric acid to remove copper (as copper sulphate). The residue is heated at 300° in hydrogen, obtained from water-gas. At this temperature ferric oxide is not changed, but nickel oxide is reduced to nickel. Carbon monoxide is next passed over the residue at the ordinary temperature, when nickel carbonyl, $Ni(CO)_4$, is obtained. This is passed through a *decomposer* containing about nine tons of nickel pellets maintained at a temperature of 180°C. The pellets are kept in constant motion so as to prevent them from cementing together, and as the nickel carbonyl decomposes (into nickel and carbon monoxide), nickel of a high degree of purity,—99·8 per cent.—is deposited round the pellets. The latter gradually grow into marbles of perfectly spherical shape. They are drawn off from time to time and screened, so that the smaller sizes may be returned to the decomposer for further growth.

The carbon monoxide produced in the decomposer is used to convert a fresh quantity of nickel into the carbonyl.

Another important method for the extraction of nickel is the Orford process. We cannot describe it here, but it is worth noticing that it involves the use of sodium sulphate, and that increasing supplies of this are being obtained from the lake deposits of Western Canada (p. 124).

A few of the chief properties of metallic nickel have already been given at the beginning of this chapter, where they are compared with those of iron and cobalt. The pure metal is now being largely used in the manufacture of tanks, boilers, tubes, etc., forming parts of chemical plants, of dishes, crucible tongs, etc., for the laboratory, and of spoons and other articles for domestic use.

Alloys.—Nickel steel has already been described (p. 185). *German silver* is an alloy of copper, nickel, and zinc. For coinage purposes, nickel is usually alloyed with about 75 per cent. of copper, but this percentage is sometimes much less.



By courtesy of Berndorf Metal Works.

Nickel Strip: approximate dimensions—length 62 feet, width 28 inches, thickness ·02 inches.

Nichrome (the name is compounded from those of its constituent metals, nickel, iron, and chromium) has a very high melting point and is used for electrical resistance heaters.

Monel metal contains about 67 per cent. of nickel, 28 of copper and 5 of iron and other elements. It has been called a "natural alloy" because the constituents are present in nearly the same proportions as they occur in the ore and are not separated during the refining process. Owing to its great tensile strength, resistance to corrosion, and other useful properties, it has a great range of uses, *e.g.* as turbine blades for use with super-heated steam, and as material for the vessels and other apparatus used in chemical manufacturing processes.

Questions

1. In what forms does iron occur in nature? Describe how the metal is extracted, giving equations to illustrate the chemical changes which take place.

2. Steel containing phosphorus would be *cold-short, i.e.* brittle at ordinary temperatures. Explain how the phosphorus is removed, giving equations if possible.

3. Distinguish between cast iron, wrought iron, and steel, (*a*) in composition, (*b*) in properties.

4. Give some account of the special kinds of steel that have been produced in recent years.

5. What is the difference between ferrous compounds and ferric compounds? Give the formulae for,—ferrous chloride, ferric chloride; ferrous nitrate, ferric nitrate; ferrous sulphate, ferric sulphate; ferrous oxide, ferric oxide; ferrous hydroxide, ferric hydroxide.

6. Describe how you would prepare from metallic iron (*a*) crystals of ferrous sulphate, (*b*) ferrous sulphide, (*c*) a solution of ferric chloride.

7. Calculate the percentage of iron in hæmatite, Fe_2O_3, and in magnetite, Fe_3O_4.

8. A man wishes to prepare 8 oz. of jeweller's rouge, Fe_2O_3. What weight of crystallized ferrous sulphate, $FeSO_4 . 7H_2O$, will it be necessary to heat?

9. A brown compound was found to have the following percentage composition: Iron, 59·9; oxygen, 25·7; water, 14·4. Find its simplest formula. What is the compound?

10. Among the nickel compounds found at Sudbury, Ont., is *nickel ochre*, $Ni_3(AsO_4)_2 . 8H_2O$. Assuming that the pure compound were available in quantity, what weight of it would be required to yield one ton of nickel?

11. What volume of carbon monoxide, measured at 21°C. and 76 cm. pressure, would be required for the conversion of 1 kilogram of nickel into nickel carbonyl? (See note in italics, p. 20.)

12. The properties of iron, cobalt, and nickel show certain resemblances which justify us in regarding the metals as forming a single family. Give as many of these similar properties as you can.

13. Mention as many ways as you can in which iron (including steel) is prevented from rusting. Your answer should include methods suitable for preventing the rusting of (*a*) a large iron bridge, (*b*) a pail, (*c*) a carpenter's tools (chisel, saw, etc.), (*d*) the containers used for holding condensed milk, ''canned'' salmon, etc., (*e*) stove-tops and lids.

14. To prevent rusting, iron is sometimes covered with a thin coating of zinc (''galvanized iron''), sometimes with one of tin. Assuming that in each case a little of the coating has worn off, show that the mischief, *i.e.* the removal of the protecting metal, may be expected to spread faster in one case than in the other. (*Hint.*—The metals, *e.g.* zinc and iron, are often in contact with a weak acid, consisting of rain-water containing dissolved carbon dioxide. Regard such a system as a voltaic cell—*cf.* Fig. 7, p. 50—and with the help of the electrochemical series decide which metal would go into solution.)

CHAPTER XVII

COPPER AND SILVER

Copper, silver, and gold are the elements of family B in Group I. They are low down in the electrochemical series (p. 51) and so are easily displaced from their compounds by other metals, and are often found free in nature. Hence they have been known from the earliest times and have long been used for coinage and for ornamental purposes. They are very malleable and ductile and are the best electrical conductors of all the metals.

In striking contrast with their neighbours, the alkali metals of family A, they are chemically rather inactive,—gold decidedly so. Thus, air and water which act so vigorously on the alkali metals have little action on them,—and, in the case of gold, no action at all.

They resemble the alkali metals in the fact that they are univalent, but copper may also be divalent; gold may be trivalent. The chlorides CuCl, AgCl, and AuCl are all insoluble in water.

In this chapter we shall consider only copper and silver, leaving gold to be considered in Chapter XIX.

Copper

History.—The use of copper coincides with one of three long chapters in the history of the human race. In the Stone Age men used tools and weapons made of flint. Later they used bronze, an alloy consisting of copper together with a little tin. The Stone Age and the Bronze Age finally gave place to the Iron Age.

Copper is found in the metallic condition in various parts of the world. Further, some of its ores are very easily

reduced to the metal. It is not surprising, therefore, to find that copper has been in use from very ancient times, and specimens of cast copper have been found in Egypt dating from about B.C. 4000. The Greeks and Romans obtained their copper from the island of Cyprus, and called it *aes cyprium* (*i.e.* Cyprian brass). *Aes cyprium* was shortened to *cyprium*, which finally became *cuprum*.

It was probably by a lucky accident that some ancient coppersmith found that if a little tin were added to the copper, the metal was hardened and made much more useful for all sorts of purposes. It is certain that bronze was worked as early as B.C. 2500, and possibly much earlier.

Occurrence.—Although uncombined copper is fairly widely distributed, it is only to the south of Lake Superior that it occurs in really large quantities. Oxides and carbonates are found, but the commonest copper ore is *copper pyrites*, $CuFeS_2$. This occurs in various parts of the world, and there are very large deposits in Canada.

Extraction.—If the ore contains only copper oxide (or hydroxide or carbonate, which on heating are converted into the oxide), it is mixed with anthracite, and on heating the mixture the ore is readily reduced ($CuO + C \rightarrow Cu + CO$).

Most copper ores, however, are *sulphides*, iron usually being present in addition, and the treatment is much more complicated. In broad outline it is somewhat as follows.

The ore is first roasted under such conditions as to oxidize the iron but not the copper,—

$$4CuFeS_2 + 9O_2 \rightarrow 2Cu_2S + 6SO_2 + 2Fe_2O_3.$$

The roasted ore is then mixed with some form of silica and melted in a reverberatory furnace (Lat. *reverbero* = I beat back). The diagram shows how the flames are "beaten back" by the roof so as to play upon the ore. In Canada, however, these furnaces are now fired by powdered coal which is blown into them. The result is that the oxide of iron is converted into silicate, which is run off as a fusible slag, leaving cuprous sulphide (*matte*).

The matte while still molten is run into a slightly modified form of Bessemer converter. This is a steel vessel lined with magnesite ($MgCO_3$), so arranged that a blast of air

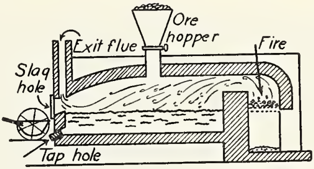


FIG. 32.—Reverberatory Furnace.

entering a little way above the bottom can be blown through the molten matte. Part of the cuprous sulphide is converted into oxide, which then reacts with more unchanged sulphide to produce copper—

$$2Cu_2S + 3O_2 \rightarrow 2Cu_2O + 2SO_2.$$
$$2Cu_2O + Cu_2S \rightarrow 6Cu + SO_2.$$

The metal which results is known as "blister copper" owing to the appearance imparted to it by the escaping gases.

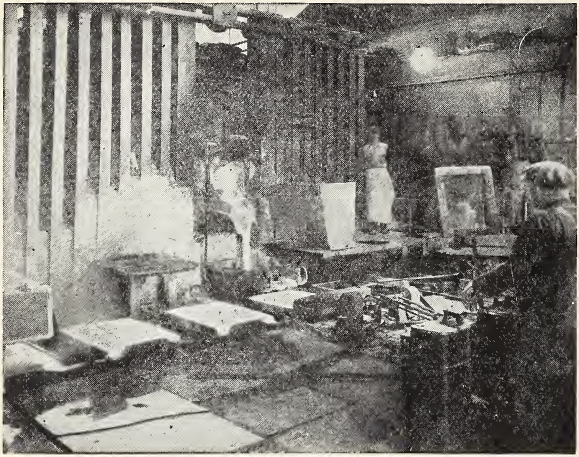
Refinement by Electrolysis.—At the present time very large quantities of copper are used for making electric cables, because *pure* copper is an excellent conductor of electricity. Its conductivity is greatly reduced, however, by the presence of very small amounts of impurity. Hence there is a great demand for copper of a high degree of purity.

Accordingly, the copper obtained by the various processes already mentioned is refined electrolytically. A bath of acidified copper sulphate solution is used, and the anode consists of a block of impure metal, which has been run out from the refining furnace (see illustration), while a thin plate of pure copper forms the cathode.

The action which takes place is briefly as follows:—

(i) Copper sulphate in solution ionizes into Cu^{++} and SO_4^{--}

(ii) Cu^{++} is immediately attracted to the cathode where it loses its electric charge, and is there deposited as an ordinary copper atom, Cu. (iii) SO_4^{--} is attracted to the anode, and



By courtesy of Anaconda Copper Mining Co.

Pouring anodes from refining furnace.

loses its charge, becoming SO_4 for a moment. "SO_4", however, apart from an electric charge, cannot exist, so it at once combines with an atom of copper from the anode, forming a molecule of $CuSO_4$, which goes into solution.

The net result is that for every atom of copper deposited on the cathode one is removed from the anode (just as though copper *travelled* from one to the other), while the solution remains of constant strength. About 80 per cent. of the world's output of copper is now electrolytically refined.

Among the impurities which settle to the bottom of the bath (the "anode mud") are small quantities of **silver**

and gold, and the value of these is often sufficient in themselves to pay for the cost of refining.

Properties and Uses.—Copper is very malleable and ductile; it possesses great tensile strength, and it is not readily corroded. These properties cause it to be used, in the form of sheet and wire, for a great variety of purposes. With the exception of silver, it is the best conductor of heat of all the metals, and is, therefore, a very suitable metal for kettles, evaporating pans, etc. The use of copper for making electric cables has already been mentioned. Even at very high temperatures it is not acted upon by steam, and it is, therefore, a very suitable metal for pipes intended to convey steam, and notably for the condenser pipes of locomotives.

The action of nitric acid and of hot concentrated sulphuric acid will have been considered in connection with the oxides of nitrogen and sulphur dioxide. The other common acids have little action.

Copper forms some extremely useful alloys, *e.g.* the various *brasses* (copper + zinc), *bronzes* (copper + tin), monel metal (chiefly copper + nickel), and nickel silver (copper + zinc + nickel).

Compounds of Copper.—Like mercury, copper forms an *-ous* series of compounds (valency, 1) and an *-ic* series (valency, 2). We have, for instance, cuprous chloride, $CuCl$, and cupric chloride, $CuCl_2$. We met with cuprous sulphide, Cu_2S, in connection with the extraction of copper from its ores. If no special termination is used (*e.g.* "copper sulphate") the *-ic* compound is understood.

Cupric Oxide, CuO, is easily prepared in the laboratory by dissolving copper in nitric acid to make the nitrate, and then evaporating to dryness, afterwards heating until brown fumes cease to be evolved—

$$2Cu(NO_3)_2 \rightarrow 2CuO + 4NO_2 + O_2.$$

Remember that copper oxide is not easily prepared by heating copper. The metal quickly oxidizes, but *only on the surface,* and the surface layer then protects the metal underneath from further action.

As copper is low down in the electrochemical series we should expect its oxide to be easily reduced,—and so it is. It is quickly reduced, for instance, by heating it in a stream of hydrogen or coal-gas.

Cupric oxide is black, but a reddish-brown compound known as cuprous oxide also exists.

Both oxides are used in the preparation of coloured glass. Cupric oxide is used to impart a blue colour, and cuprous oxide to impart a red one.

Copper Sulphate, $CuSO_4 . 5H_2O$, (strictly cupr*ic* sulphate), is often known as *blue vitriol* or *blue-stone*. On the large scale it is manufactured by the action of dilute sulphuric acid on copper in the presence of air—

$$[Cu + H_2SO_4 + O \rightarrow CuSO_4 + H_2O]$$
$$2Cu + 2H_2SO_4 + O_2 \rightarrow 2CuSO_4 + 2H_2O.$$

It crystallizes out with five molecules of water of crystallization. We often make use of the fact that copper sulphate which has been *dehydrated* on gently heating, regains its water of crystallization when water is added to it. The change of colour, from white to blue, makes copper sulphate a useful reagent for the detection of water.

On adding a *little* ammonia to copper sulphate solution, a blue precipitate of copper hydroxide is obtained. This readily dissolves in excess of ammonia yielding a solution of beautiful blue colour, containing the divalent positive ion cuprammonium, $Cu(NH_3)_4$, the salt present being, in fact, cuprammonium sulphate, $Cu(NH_3)_4SO_4$. By slightly varying the procedure—filtering and washing the copper hydroxide before dissolving in ammonia—we obtain a solution of cuprammonium *hydroxide*, $Cu(NH_3)_4(OH)_2$. This solution possesses the very curious property of dissolving cellulose (filter paper, cotton-wool, etc.). By squirting the cellulose solution into dilute acid, a thread of amorphous cellulose is obtained, and this reaction forms the basis of one method of manufacturing artificial silk.

A mixture of copper sulphate and lime is known as *Bordeaux mixture*, used in the garden for destroying insect pests, etc.

Copper sulphate is much used where copper electroplating is being done, and we have a good example in the making of electrotypes, or "electros" as the printer calls them. It is often necessary to obtain duplicates of type which has been "set up", because if a very large number of copies were printed off the original type, the latter would become worn and the print obtained from it would be blurred.

To obtain a duplicate, the type as originally set up is pressed upon a bed of plaster, a mould being thus obtained. The mould is dusted over with powdered graphite, which is a good conductor of electricity. The "black-leaded" mould is now hung as cathode in a bath of acidified copper sulphate solution, a plate of copper being made the anode. Copper is deposited until a thickness of about $\frac{1}{16}$th inch has been obtained. After this the copper deposit, which is an exact reproduction of the original type, is carefully stripped off, and backed with type metal.

Copies of medals and many other objects may be made in a similar way.

Tests for Copper Ion.—There are many good tests for copper ion, some of which have been referred to incidentally in the foregoing two or three pages.

(1) Copper salts give a green or blue colour to the flame.

N.B.—Hence the blue colour seen when salt is thrown into a clear fire. The coal contains traces of copper compounds, and, on adding salt, a little copper chloride is formed. This salt, being very volatile, at once gives the characteristic colour to the flame.

(2) Copper salts give a blue solution.

(3) Hydrogen sulphide gives a black precipitate, *e.g.*—

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4.$$

(4) A pen-knife, bright iron nail, etc. if dipped into a solution of a copper salt, becomes coated with copper.

(5) On adding ammonia, a blue precipitate is obtained, or (with excess of ammonia) a deep blue solution.

Silver

Silver occurs most commonly as *argentite* (or *silver glance*) Ag_2S, often associated with galena (PbS). **It is**

sometimes found in the free condition, *e.g.* in the Cobalt district of Ontario, where the uncombined silver is mixed with cobalt and other ores including argentite.

Canada is at present the third silver-producing country in the world, Mexico coming first and the United States second. Most of the Canadian output comes from British Columbia, Ontario and Quebec.

Extraction.—There are many methods of extraction depending chiefly on the form in which the silver occurs, but only one or two can be indicated here. Native silver is sometimes simply hand-picked and melted down, though further purification may be necessary. At Cobalt the ore is first concentrated and finely ground. At this stage it consists chiefly of argentite and free silver. It is then treated with a 0·7 per cent. solution of sodium cyanide, and the slime is thoroughly agitated with a stream of air. The result is that a solution of sodium argentocyanide $NaAg(CN)_2$ is formed—

$$4Ag + 8NaCN + 2H_2O + O_2 \rightarrow 4NaAg(CN)_2 + 4NaOH.$$

By the addition of sodium sulphide the silver is now precipitated from solution as silver sulphide—

$$2NaAg(CN)_2 + Na_2S \rightarrow Ag_2S + 4NaCN.$$

By courtesy of the Ontario Dept. of Mines.

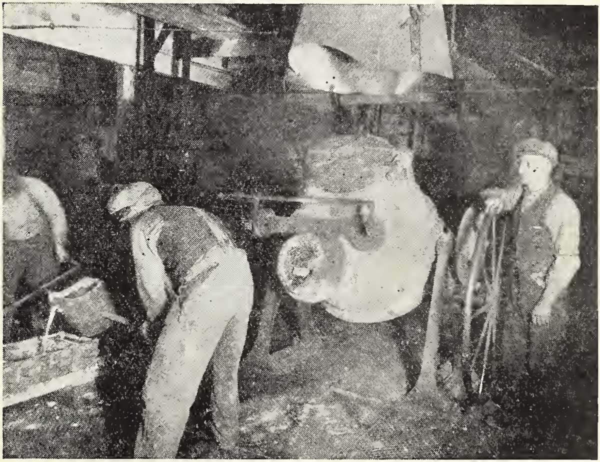
Specimen of polished ore from the Miller Lake O'Brien Mine, Gowganda. Note fern-like structure of crystallized native silver (bottom), cobalt-iron arsenides (centre), enclosed in calcite gangue (dark). The illustration is half natural size.

Finally, the silver sulphide is placed in a revolving cylinder and reduced by the action of caustic soda and aluminium—

$$2Al + 2NaOH + 2H_2O \rightarrow 2NaAlO_2 + 3H_2.$$
$$Ag_2S + H_2 \rightarrow 2Ag + H_2S.$$

Note that silver is the only solid product and is, therefore, easily separated. From the solution of sodium aluminate, $NaAlO_2$, alumina (Al_2O_3) is readily obtained and is used for extraction of aluminium in the usual way.

If specially pure silver is required it is refined electrolytically, the cathode being a thin plate of pure silver; a block of the unrefined material forms the anode. The bath consists of a solution of silver nitrate. Copper is a very common impurity and this passes into solution, while gold forms as a slime and is collected in a canvas bag placed round the anode.



(*By courtesy of Deloro Smelting and Refining Co., Limited.*)
Pouring silver.

Incidentally we may notice that practically the same process serves for electroplating, but in this case the bath usually consists of potassium argento-cyanide, KCN . AgCN, while the cathode consists of the article to be plated.

Properties.—Silver is a lustrous white metal, of density 10·5 and melting at 956°. Of all the metals it is the best conductor of heat and electricity, and with the exception of gold it is also the most malleable and ductile. conducts heat.

It is not acted upon by pure air, but it tarnishes in air containing traces of hydrogen sulphide, silver sulphide being produced. If a silver spoon is used in egg or mustard it tarnishes for the same reason, both these substances containing compounds of sulphur.

It is very resistant to the action of alkalies even when the latter are fused, and so silver crucibles are used for certain operations in the laboratory.

As silver is low in the electrochemical series it is easily obtained from its salts by reduction, and by making use of this property we can obtain a silver mirror. Some dilute silver nitrate is poured into a test-tube which has been thoroughly cleaned. Sodium hydroxide is added, giving a brown precipitate of silver oxide, and this is *just* re-dissolved by the addition of dilute ammonia. A solution of Rochelle salt (a reducing agent) is now added. On gently heating, the test-tube is soon coated with a brilliant silver mirror.

When used for coinage, ornamental articles, etc., silver is usually alloyed with a little copper to make it harder. To " assay " silver, *i.e.* to find what percentage of it is present in a given specimen, a small quantity of the latter is weighed and placed in a bone ash crucible called a *cupel.* A little lead is added, and the cupel is then strongly heated with free access of air. Any copper present is oxidized; the copper oxide dissolves in the lead oxide; and the latter, which is easily fusible, is absorbed by the bone ash of the cupel. The button of pure silver which remains is then weighed, and this represents the weight of silver in the specimen taken.

Silver Nitrate, $AgNO_3$, is made by dissolving silver in nitric acid and crystallizing out When strongly heated, it decomposes and silver is left—

$$2AgNO_3 \rightarrow 2Ag + 2NO_2 + O_2.$$

In the laboratory, silver nitrate solution is most often used in testing for a chloride. On adding it to a solution of sodium chloride, for instance, a white precipitate of silver chloride is obtained, insoluble in nitric acid but soluble in ammonia—

$$AgNO_3 + NaCl \rightarrow AgCl + NaNO_3.$$

The test for bromides and iodides is very similar to that for chlorides.

Silver nitrate in the form of thin sticks is sold by the druggist under the name of *lunar caustic.* It has a destructive action on flesh and is sometimes used for removing warts, cauterizing wounds, etc. In contact with organic matter such as linen, skin, cork, etc., silver nitrate is soon decomposed, giving a black deposit of silver. For this reason it is a common constituent of marking inks.

Silver Chloride, AgCl.—You have probably met with this as the white precipitate obtained in testing for a chloride. Conversely, we test for silver by adding dilute hydrochloric acid ("Group I" in analysis).

On a bright sunny day we notice that the white precipitate soon turns to a delicate violet. On a dull day the change is much slower.

Silver Bromide, AgBr.—This is obtained as a pale yellow precipitate on adding a solution of silver nitrate to one of a bromide. Like silver chloride, it is insoluble in nitric acid but it is only slightly soluble in ammonia.

In a medium of gelatine, silver bromide is much used in photography. Gelatine and potassium bromide are dissolved in hot water, and silver nitrate is added, giving a precipitate of silver bromide dispersed throughout the gelatine. The emulsion is poured on the glass or celluloid according as "plates" or "films" are being prepared, and the deposit is allowed to dry.

Photography.—There is still some uncertainty as to exactly what happens when a sensitive plate is "exposed" in a camera, but when the plate is afterwards "developed" it is found that the extent to which the silver bromide can be reduced to silver depends on the amount of light to which it has been exposed. Thus, if A has received much light, C none at all, and B an intermediate amount, we find on developing that at A we get a thick deposit of silver and at C none at all, while at B there would be a thin deposit. Instead of showing only the three stages, however, a correctly-exposed plate would show hundreds.

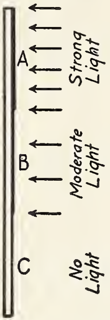


Fig. 33—Action of light on sensitive plate.

A number of developers are in common use, but hydroquinone, $C_6H_4(OH)_2$, (in alkaline solution) will serve as a typical example. As it reduces the silver bromide to silver, it is itself oxidized to quinone, $C_6H_4O_2$ —

$$C_6H_4(OH)_2 + 2AgBr \rightarrow 2Ag + 2HBr + C_6H_4O_2.$$

Over-vigorous development would cause reduction of some of the silver bromide which has not been acted upon by the light, and the result would be general "fogging" of the plate. To prevent this, potassium bromide is added to act as a "restrainer".

After developing, it is necessary to remove all unchanged silver bromide, and this is done by "fixing" in a bath of sodium thiosulphate ("hypo")—

$$AgBr + Na_2S_2O_3 \rightarrow NaAgS_2O_3 + NaBr.$$

The sodium-silver thiosulphate, $NaAgS_2O_3$, and the sodium bromide are both soluble, so the plate now contains nothing but a deposit of silver, of thickness varying according to the amount of light received from the original object. Bright parts of the object are represented by a thick deposit and vice versa, so that in the *negative* as it is called "light appears dark and dark appears light".

To obtain a print, a piece of light-sensitive paper is placed behind the negative, which is then exposed to light. If the silver is dense at A and there is no silver at all at C, it is clear that the paper behind A will receive very little light while that behind C will receive a good deal. Thus the dark and light parts of the negative are reversed in the print, and the latter therefore reproduces the lighting of the original object.

"Toning" consists in replacing the silver image with a gold one, which produces a more pleasing effect. It is done by putting the silver print in a bath in which gold chloride ($AuCl_3$) is dissolved. As gold is even lower than silver in the electrochemical series, it is displaced from solution ($AuCl_3 + 3Ag \rightarrow 3AgCl + Au$). The print is afterwards well washed to remove the silver chloride.

Questions

1. A number of the properties of copper and silver depend on the fact that they occupy a low position in the electrochemical series (p. 51). Give as many of these properties as you can.

2. How would you find the percentage of copper in cupric oxide and cuprous oxide respectively?
   In a careful experiment the first percentage was found to be 79·9 and the second 88·8. Show that these numbers are in accordance with the law of Multiple Proportions.

3. An ore, known as *ruby-silver,* is found when carefully purified to have the following percentage composition:— silver, 59·8; antimony, 22·5; sulphur, 17·7. Find its simplest formula.

4. Account for the fact that a solution of copper sulphate is acid to litmus paper.

5. How would you prepare a specimen of (*a*) copper from copper sulphate, (*b*) copper sulphate from copper?

6. Assuming that silver nitrate when heated decomposes according to the equation on p. 207 and that the gases are collected at 150°C. and 77 cm. pressure, what volume of the mixed gases should be obtained by heating 3·4 gm. of silver nitrate? (The gram-molecule of any gas at N.T.P. occupies 22·4 litres.)

CHAPTER XVIII

TIN AND LEAD

FAMILY B of Group IV consists, in ascending order of atomic weight, of carbon, silicon, germanium, tin, and lead, —the element germanium being extremely rare. At first sight there seems to be no resemblance between carbon on the one hand and tin and lead on the other, but at least they all form oxides of the type RO and RO_2, and we shall see a few other points of resemblance presently.

Tin and lead resemble one another rather closely in some of their physical properties, and among their compounds lead tetrachloride, $PbCl_4$, somewhat resembles stannic chloride, $SnCl_4$.

Tin

Occurrence.—Tin occurs in several countries of the world, chiefly Bolivia and the Malay States, as *tinstone* SnO_2, from which the metal is obtained by reduction with fine coal ($SnO_2 + 2C \rightarrow 2CO + Sn$). It is often purified by *liquation*, for, on gently heating, the tin, which has a low melting point (232°), flows away from the impurities present.

Properties and Uses.—Tin is not attacked by air or water, and it is therefore very largely used for covering sheets of iron, which are thus made into *tin-plate.* This contains about 2 per cent. of tin, and is made up into " tins " of every shape and size to contain cocoa, tobacco, and a host of other things.

In making tin-plate, the sheet iron is first thoroughly cleaned, and is then dipped into a bath of the molten metal. It is afterwards put through rollers to remove superfluous metal—at $800 a ton, tin is much too good to be wasted.

Incidentally we may notice that *detinning,*—the recovery of tin from scrap tin-plate,—is a regular industry. After being thoroughly cleaned, the scrap metal is packed into iron cylinders into which chlorine is passed. This converts the tin into stannic chloride $SnCl_4$, a liquid boiling at 114°. The remaining scrap iron is made into blocks by hydraulic pressure, and re-smelted by the open-hearth process.

Tin could easily be recovered from stannic chloride, but in practice the chloride is converted, by treatment with water, into the crystalline hydrate $SnCl_4 . 5H_2O$, for which there is a good demand in the dyeing industry.

Tin-foil is largely used for packing chocolates, cigarettes, etc. Tin is also used for *tinning* iron and copper cooking-vessels. The vessel is first thoroughly cleaned, after which molten tin is poured into it. Resin and sal-ammoniac are added to act as a flux as in soldering, and with the help of a brush the metal is made to cover the whole surface.

Tin forms some very important alloys. Thus, with lead it forms " solder ", which is " finer " or " coarser " according as it contains a higher or lower proportion of tin. *Pewter* contains 4 parts of tin, 1 of lead, and (usually) a little antimony. Bronze (gun-metal) and bell-metal are both alloys of copper and tin.

The " backing " of mirrors consists of tin-amalgam, *i.e.* an alloy of tin and mercury.

Below 18°C. tin shows a tendency to change into an allotropic form, a powder known as *grey tin.* The change takes place most rapidly at —50°C.

In 1912 this change was partly responsible for the disaster which overtook five members of a Polar expedition. Captain Scott and four companions were returning from the South Pole. On this return journey they picked up, at intervals of every few miles, supplies of food and oil which they had deposited on their outward journey. The whole party perished. Captain Scott's diary, found by the side of his dead body, contains many references to the fact that his oil supplies were nearly always short of the

amount he expected to find, and this shortage was one cause of the disaster. There is little doubt that, at the low temperatures which prevailed, the containing vessels had become leaky through the tin with which they were coated having been turned into the powdery grey variety.

Oxides.—Tin forms two oxides, stannous, SnO, and stannic, SnO_2,—of which the latter is much the more important. We have already seen that it occurs native, and is the source from which tin is obtained on the large scale. It is a white powder which, like zinc oxide, becomes yellow while hot, but regains its white colour on cooling. It has feebly acidic properties, and when fused with caustic soda forms sodium stannate, Na_2SnO_3—

$$SnO_2 + 2NaOH \rightarrow Na_2SnO_3 + H_2O.$$

In this respect it shows a resemblance to carbon dioxide. It is insoluble in acids, and, in fact, shows practically no sign of basic properties.

Stannous oxide is a black powder obtained by heating stannous oxalate out of contact with air —

$$SnC_2O_4 \rightarrow SnO + CO + CO_2.$$

On exposure to the air it burns, forming the dioxide. In the readiness with which the monoxide passes into the dioxide we have another point of resemblance to carbon.

Stannous oxide is amphoteric (*cf.* aluminium oxide) for it can function both as a base giving rise to stannous salts (*e.g.* the sulphate, $SnSO_4$) and as an acidic oxide giving rise to stannites (*e.g.* sodium stannite, Na_2SnO_2).

Chlorides.—Stannous chloride, $SnCl_2$, is formed when tin is dissolved in concentrated hydrochloric acid—

$$Sn + 2HCl \rightarrow SnCl_2 + H_2.$$

It crystallizes out as $SnCl_2 . 2H_2O$, and, on heating, this loses hydrochloric acid as well as water, a basic salt being formed. The anhydrous chloride may, however, be made by passing a stream of dry hydrogen chloride over heated tin.

On heating with water, stannous chloride is partially hydrolysed, an insoluble basic chloride being produced—

$$2SnCl_2 + 2H_2O \rightleftarrows SnCl_2 \cdot Sn(OH)_2 + 2HCl.$$

Now, in preparing a solution of stannous chloride we wish to make the above reaction go from right to left, so we always add hydrochloric acid. A quantity of tin should afterwards be put into the bottle to prevent subsequent oxidation to stannic chloride, $SnCl_4$.

Stannous chloride is used in the laboratory chiefly in testing for a mercuric salt. If we use a *little* of the stannous salt a white precipitate of mercurous chloride is produced. If we use more, a grey precipitate of metallic mercury is produced, especially on warming. The equations would be—

$$2HgCl_2 + SnCl_2 \rightarrow SnCl_4 + Hg_2Cl_2,$$

and $$Hg_2Cl_2 + SnCl_2 \rightarrow SnCl_4 + 2Hg.$$

The preparation of stannic chloride, $SnCl_4$, from tin and chlorine, has already been mentioned in connection with detinning.

Lead

Occurrence and Extraction.—Lead is found in many parts of the world, chiefly as *galena*, PbS. Large deposits occur in Canada, especially in British Columbia, which in 1930 produced over 150,000 tons of lead. Here the galena is associated with other sulphides, notably of zinc and iron, and an approximate separation is first effected by elaborate froth-flotation methods (p. 109). The concentrated lead ore is now placed on the floor of a furnace to which air is admitted. The result is that:—

(1) Some of the galena is oxidized to sulphate—

$$PbS + 2O_2 \rightarrow PbSO_4.$$

(2) Some of it is converted into oxide—

$$2PbS + 3O_2 \rightarrow 2PbO + 2SO_2$$

(3) Some of it is not changed at all.

The *sinter,* as the roasted product is called, is now mixed with coke and a flux consisting of iron pyrites, and transferred to a small blast furnace. Here the pyrites is first changed to ferric oxide ($2FeS_2 + 11O \rightarrow Fe_2O_3 + 4SO_2$), and the ferric oxide is reduced to iron as already described in Chapter XVI. A number of reduction processes now take place, causing the lead sulphide, sulphate, and oxide all to be reduced to lead. The sulphide is reduced by the iron already mentioned ($PbS + Fe \rightarrow FeS + Pb$), the sulphate by another portion of the sulphide,

$$PbSO_4 + PbS \rightarrow 2SO_2 + 2Pb,$$

and the oxide by the coke ($PbO + C \rightarrow Pb + CO$).

The lead is now cast into anodes each weighing 375 lb. and purified by electrolysis.

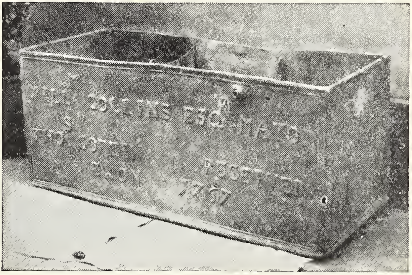
The blast furnace slag still contains a considerable amount of lead (and zinc). It is, therefore, treated in batches of 50 or 60 tons at a time with a blast of air and coal dust. The latter burns fiercely and heats the slag, vaporizing the zinc and lead. Then the excess of air in the blast oxidizes them, and the oxides are conveyed into flues and so recovered. By treatment with sulphuric acid the zinc oxide is extracted as sulphate, and passed on for electrolysis (p. 160), while the insoluble lead oxide residues are re-smelted.

Properties.—Freshly-cut lead has a silvery, slightly bluish surface, but it soon becomes dull owing to the production of a film of carbonate (the oxide first formed reacting with atmospheric carbon dioxide). This carbonate protects the lead beneath from further change, with the result that articles made of lead are wonderfully little affected (except on the surface) by exposure to the atmosphere. Thus, the photograph shows a cistern which was made nearly 200 years ago, and is little the worse for wear. Even more striking is the fact that many of the lead pipes

which the Romans used at Bath nearly 2000 years ago are still doing their work perfectly well.

Pure water with oxygen in solution has a perceptible effect on lead. The dissolved gas first oxidizes the metal, and the lead oxide is then converted into lead hydroxide, which is slightly soluble ($PbO + H_2O \rightarrow Pb(OH)_2$).

Now, soluble lead compounds are poisonous, so it looks as though it would be dangerous to drink water which has passed through lead pipes. In practice the difficulty very seldom arises. Ordinary drinking water is never perfectly "soft"—it contains at least a little calcium sulphate and bicarbonate in solution (p. 147). The result is that the lead pipes become coated with a thin film of lead sulphate



18th century lead tank in the Rougemont Gardens, Exeter, (England).

and lead carbonate, and this film forms a perfect barrier between the water on one side and the lead on the other.

Lead is very resistant to the action of hydrochloric and sulphuric acids, and this may be due in part to the fact that it is only *just* above hydrogen in the electromotive series; but the chief cause is no doubt the insolubility of lead chloride and lead sulphate. You will remember that the chambers used in the manufacture of sulphuric acid are made of this metal. Lead dissolves easily when warmed with

nitric acid, lead nitrate being produced and oxides of nitrogen (nitric oxide predominating if the acid is dilute, nitrogen peroxide if it is concentrated; the similar reactions with copper will be familiar). Its low melting point (327°C.) is often a useful property, *e.g.* in plumbers' repair work, and in the making of shot. It forms many useful alloys, to which it imparts this same property. Examples are pewter and solder (already mentioned under "Tin"), type metal, and the various "fusible alloys".

Uses.—Some of these have already been indicated, but there are many others. Among them we may mention its use in storage batteries and as a casing for cables of all kinds; also in making sporting ammunition and lead foil. It is used too, in making important substances such as white lead and red lead. In fact, the annual world consumption of lead is in the neighbourhood of two million tons.

Oxides of Lead.—Five oxides of lead are known, and of these we must consider three.

Lead monoxide ("litharge"), PbO, is the yellow or reddish-yellow substance formed when lead is heated in air. Traces of it can be seen in the plumber's melting-pot when street pipes are being repaired. It has many uses, one of which is in the glazing of pottery (p. 96). It is also used in making flint-glass.

Lead oxide is often added to paint to speed up the process of "drying". The drying really consists in the combination of the linseed oil with atmospheric oxygen, a solid compound called "linoxyn" being formed. The lead oxide acts as a catalyst.

The monoxide is the most stable oxide of lead, and is formed when any of the other oxides are strongly heated.

Red lead, Pb_3O_4,[1] is made by heating the monoxide in air at a temperature of about 400°C.

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[1] The percentage of oxygen in ordinary specimens of red lead differs considerably from that required by the formula Pb_3O_4.

$[3PbO + O \rightarrow Pb_3O_4]$ $6PbO + O_2 \rightarrow 2Pb_3O_4$.
At a somewhat higher temperature (470°) the action is reversed.

When warmed with dilute nitric acid, red lead at once turns brown owing to the formation of lead dioxide. On filtering, the dioxide remains behind, while lead nitrate passes through and can easily be crystallized out.

To arrive at the equation, it is best to regard Pb_3O_4 as $2PbO + PbO_2$. We may then suppose that the monoxide PbO reacts in the ordinary way to form the nitrate, while the dioxide PbO_2 is unchanged, *i.e.*

$$PbO + 2HNO_3 \rightarrow Pb(NO_3)_2 + H_2O \qquad (a)$$

or

$$2PbO + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + 2H_2O \qquad (b)$$

$$PbO_2 \rightarrow PbO_2 \qquad (c)$$

Adding (*b*) and (*c*),

$$Pb_3O_4 + 4HNO_3 \rightarrow 2Pb(NO_3)_2 + PbO_2 + 2H_2O.$$

Like the monoxide, red lead is used in making flint glass. It is also much used as a red paint.

Lead dioxide or *peroxide*, PbO_2, may be prepared as indicated above. It is interesting to notice that it is also produced during the electrolysis of dilute sulphuric acid, using a lead anode. As soon as SO_4^{--} ions are discharged at the anode, they react with the water present yielding nascent oxygen which at once combines with the lead of the anode,

i.e. (*a*) $2SO_4 + 2H_2O \rightarrow 2H_2SO_4 + 2O$,
and (*b*) $Pb + 2O \rightarrow PbO_2$.

This reaction takes place in the *storage battery* or *accumulator*, which we must now consider. In its discharged condition it consists essentially of two lead plates covered with a paste of lead sulphate, and separated from one another by dilute sulphuric acid. Fig. 34, (*a*) represents the process of *charging*, the anode (+) being connected with a dynamo or other source of direct current. Ions of SO_4^{--} are discharged at the anode, where we have the reaction

$$PbSO_4 + SO_4 + 2H_2O \rightarrow 2H_2SO_4 + PbO_2 \qquad (a).$$

Hydrogen ions are discharged at the cathode, the reaction being

$$PbSO_4 \ + \ 2H \ \rightarrow \ H_2SO_4 \ + \ Pb \qquad (b).$$

Adding (a) and (b) we get—

$$2PbSO_4 \ + \ 2H_2O \ \rightarrow \ Pb \ + \ 2H_2SO_4 \ + \ PbO_2.$$

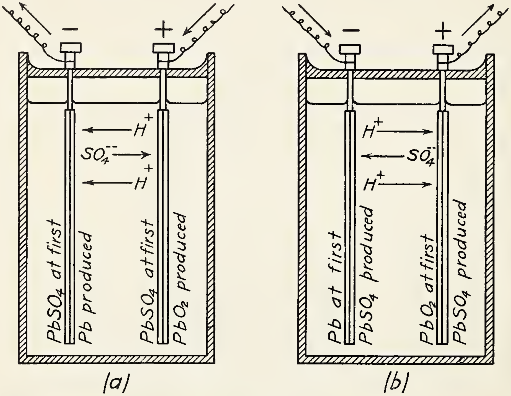


FIG. 34.—Accumulator being (a) charged, (b) discharged.

This is convenient *only as showing the final result of the chemical change,*—disappearance of lead sulphate, etc.—but we must not regard it as we do an ordinary chemical equation. Actually, if we poured water on lead sulphate, nothing at all would happen.

Going back once more to (a) and (b), we see that as charging proceeds, the coating of lead sulphate is gradually exchanged for one of lead peroxide at the anode, while it is removed entirely from the cathode. When charging is complete, the cell begins to " gas ", oxygen coming from the anode (due to the reaction $SO_4 + H_2O \rightarrow H_2SO_4 + O$) and hydrogen from the cathode.

So far the cell has obviously been *gaining* electrical energy, and certain chemical actions have been taking place at the same time. If these actions were reversed, we should expect a corresponding *loss* of energy, and if the conditions were suitable this discharge of energy might take the form of an electric current. All this,—reversed chemical action, and loss of energy expressing itself as an electric current,—all this actually happens if, after charging, we connect the poles of the cell by a wire. Lead sulphate is re-formed, and a current flows in the opposite direction to that of the charging current.

The storage battery is obviously a very convenient means of storing electrical energy in the form of chemical energy. Its uses are too well-known to need description here. In cases where it is necessary to move the battery (*e.g.* an electrically-driven truck), the weight of the lead plates is rather a serious disadvantage, and so batteries based on other reversible reactions have been constructed. So far, however, these have not met with entire success.

Action of Heat, Hydrogen, and of Hydrochloric Acid on the Oxides of Lead.—Lead monoxide is very stable. It melts when strongly heated, but undergoes no chemical change.

The other oxides easily decompose, oxygen being evolved while the monoxide is left behind. You should be able to make up the equations for yourself.

All the oxides of lead, when heated in a current of hydrogen, are readily reduced to the metal.

When heated with hydrochloric acid, lead chloride and water are formed in all cases, and except in the case of the monoxide, chlorine is evolved—

$$PbO + 2HCl \rightarrow PbCl_2 + H_2O$$
$$Pb_3O_4 + 8HCl \rightarrow 3PbCl_2 + 4H_2O + Cl_2$$
$$PbO_2 + 4HCl \rightarrow PbCl_2 + 2H_2O + Cl_2.$$

(N.B.—In writing the equations, arrange that the amount of hydrogen shall be just enough to turn all the oxygen into water, *e.g.*, with Pb_3O_4 take 8HCl.)

Lead Acetate, $Pb(C_2H_3O_2)_2 . 3H_2O$ (see p. 174 for short discussion of formula) is made by dissolving litharge in dilute acetic acid and crystallizing out.

$$PbO + 2H . C_2H_3O_2 \rightarrow Pb(C_2H_3O_2)_2 + H_2O.$$

A solution of it is often used in testing for hydrogen sulphide, with which it gives a black precipitate of lead sulphide—

$$Pb(C_2H_3O_2)_2 + H_2S \rightarrow PbS + 2H . C_2H_3O_2.$$

Lead Nitrate is easily made by the action of moderately-concentrated nitric acid on the metal or the monoxide. When heated, it decomposes into nitrogen peroxide and oxygen, and is frequently used for the preparation of liquid nitrogen peroxide —

$$2Pb(NO_3)_2 \rightarrow 2PbO + 2NO_2 + O_2.$$

White Lead has the formula $(PbCO_3)_2 . Pb(OH)_2$ and is a good example of a basic salt (p. 156). For centuries it has been made by what is now called the *Dutch process,* of which the following is a brief outline.

An earthenware pot has a ledge on the inside, and across this is placed a sheet or roll of lead, the lower half of the pot (below the ledge) containing vinegar. The pot is covered with another sheet of lead. Some scores of these pots are placed on heaps of stable manure, and after a few weeks the metal is found to have been converted into white lead.

There is some doubt as to the chemical changes that take place, but the following explanation seems reasonable.

First of all, the manure acts by keeping the pots warm, and by giving off carbon dioxide. Then
(*a*) the lead is converted into a basic acetate by the combined action of acetic acid vapour and air—

$$2Pb + 2H . C_2H_3O_2 + O_2 \rightarrow Pb(C_2H_3O_2)_2 . Pb(OH)_2.$$

(*b*) The basic acetate is decomposed by carbon dioxide and water vapour, white lead being formed and acetic acid re-produced—

$$3Pb(C_2H_3O_2)_2 . Pb(OH)_2 + 4CO_2 + 2H_2O \rightarrow 2(PbCO_3)_2 . Pb(OH)_2 + 6H . C_2H_3O_2.$$

The liberated acetic acid now attacks a fresh quantity of lead, and the process continues until there is no metal left. The product is treated with water to extract any remaining lead acetae (soluble) and the residue is then gently dried by heating under reduced pressure.

There are quick modern processes for the production of white lead, but none of them gives so good a product as that obtained by the Dutch process. The grains are too large, and so the substance has not the same covering power.

The chief drawback to white lead as a pigment has already been discussed on p. 162.

Lead Chromate, $PbCrO_4$, is a yellow, insoluble substance, obtained by adding a solution of a chromate to a solution of a lead salt, *e.g.*—

$$K_2CrO_4 + Pb(NO_3)_2 \rightarrow 2KNO_3 + PbCrO_4.$$

Hence, we may test for a lead salt by adding a solution of a chromate, and vice versa.

Lead chromate is used as a pigment under the name of *chrome yellow.*

Lead Sulphate, $PbSO_4$, is a highly insoluble compound, and is readily made by double decomposition, *e.g.* by adding a solution of lead nitrate to one of magnesium sulphate—

$$Pb(NO_3)_2 + MgSO_4 \rightarrow PbSO_4 + Mg(NO_3)_2.$$

Epsom salts (magnesium sulphate) is, in fact, one of the best antidotes in cases of lead poisoning; for besides its action as a purgative, it turns the lead into an insoluble and, therefore, comparatively harmless compound.

Lead Arsenate, of which a considerable amount is used in U.S.A. and Canada for spraying fruit-trees, etc. to get rid of insect pests, is usually prepared by suspending lead monoxide in a weak solution of arsenic acid, a small amount of nitric or acetic acid being present to act as catalyst. The normal arsenate would have the formula $Pb_3(AsO_4)_2$,

but the commercial product seems to be a mixture of several highly-complex basic arsenates (*cf*.q.11).

Questions

N.B.—See note in italics, p. 20.

1. Assume (as is very reasonable) that a few primitive men happened to make a big fire over a deposit of tinstone. Write an account of what you might very well have observed if you had been watching them.

2. In 1867 the Russian Government had received a large supply of block tin which they stored in cellars during the winter. On opening the cellars the following spring the bright tin had all disappeared, but the floor was thickly covered with a grey powder. Explain.

3. What is a basic salt? Give the names and formulae of three basic salts mentioned in the foregoing chapter.

4. Why is it particularly undesirable that stannous chloride in solution should be allowed to oxidize to stannic chloride, and how is the change prevented?
   Why should the change be called *oxidation?*

5. Can you suggest why a great sulphuric acid industry, and also a great ammonium sulphate industry, are developing in British Columbia?

6. Starting from red lead, how would you prepare specimens of lead monoxide, peroxide, nitrate, and sulphate?

7. You wish to be quite sure that the water supply is free from lead. How could you find out? (N.B.—If lead compounds are present at all, it will be in extremely dilute solution.)

8. In 1930 British Columbia produced 152,000 tons of lead. Assuming that this was originally present as sulphide, what weight of sulphur dioxide would escape into the air if no preventive measures were taken?

9. Find the simplest formula of a substance of which the percentage composition is:—lead, 80·13; carbon, 3·09; oxygen, 16·52; hydrogen, 0·26. What is the substance?

10. What volume of chlorine, measured at 16°C. and 76 cm. pressure, would be obtained by heating 30 gm. of red lead (assumed to be Pb_3O_4) with hydrochloric acid?

11. Commercial lead arsenate is said to contain a compound of the formula $Pb(PbOH)(AsO_4)_3 . H_2O$. Calculate the percentage of lead and the percentage of arsenic in this compound.

CHAPTER XIX

GOLD AND PLATINUM

Gold

Occurrence.—Gold is nearly always found in the metallic form, but containing at least a small amount of silver; sometimes copper and other metals are present. Small quantities of gold are often associated with ores of copper, lead, and other base metals, and when these reach their final stage of purification (usually by electrolysis), the gold

By courtesy of the Bureau of Mines, B. C.
Panning for Gold.

may be recovered. In British Columbia, for instance, most of the gold produced is obtained in this way.

Gold occurs in veins of quartz ("lode gold") in particles which are usually too small to be seen with the naked eye.

Some of the quartz breaks down, forming alluvial deposits, the gold being then known as " placer gold ".

As a gold-producing country Canada is at present surpassed only by South Africa. Her output in 1932 was nearly three million fine ounces, over four-fifths of this being produced by Ontario.

Extraction.—Formerly gold was extracted from the sand

By courtesy of the Bureau of Mines, B. C.

Workings on Fraser River.

and gravel of a river bed by " panning ", which consists in shaking with water and pouring off the lighter particles of sand, etc. (see illustration). This method is not much used nowadays except by prospectors.

Often an alluvial deposit is covered with a thick, hardened bed of gravel, and this is removed by "hydraulic mining",—directing on it a stream of water at very high pressure, something like 100 lb. per square inch. When the gold-bearing deposit is reached, the water carrying the gravel is made to stream through a long wooden sluice with a downward slope. The natural tendency is, of course, for the heavy gold particles to be deposited in the sluice while the gravel, etc. passes on, and this tendency is assisted by the use of mercury (to which the gold adheres) and by various mechanical devices which cannot be described here.

In the case of "lode gold" the rock must first be crushed. If local conditions (*e.g.* water supply) are suitable, much of the worthless material may be removed by mechanical means, but usually it is dealt with in mills by various methods, of which one or two may be described briefly.

Amalgamation process.—This is often combined with the sluice method described above. The crushed material is made to flow over amalgamated copper plates (*i.e.* their surface consists of an amalgam of copper and mercury). The gold is retained at the surface, partly in solution but chiefly by adhesion. The amalgam is now scraped off and distilled, the mercury being condensed and used again. The gold left behind is purified by cupellation (p. 206).

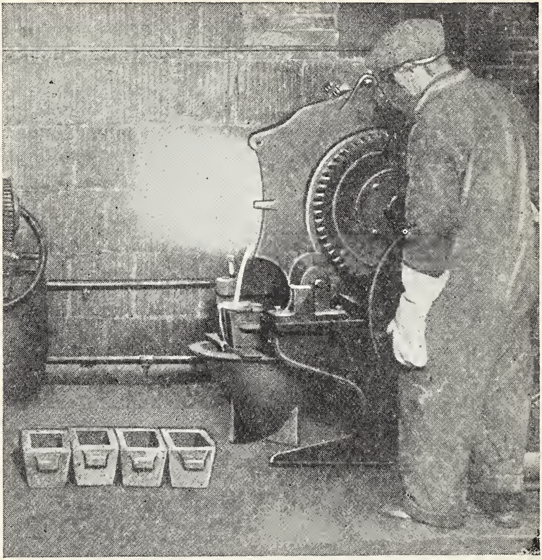
Cyanide process.—The finely-crushed ore is agitated in large tanks with a 0·3 per cent. solution of potassium or sodium cyanide. The gold dissolves forming potassium aurocyanide—

$$4Au + 8KCN + 2H_2O + O_2 \rightarrow \underset{\textit{Potassium auro-cyanide}}{4KAu(CN)_2} + 4KOH.$$

After settling, the clear solution is treated with zinc,—often the zinc containers in which the cyanide has been packed. Zinc (being much higher in the electrochemical series) replaces the gold—

$$2KAu(CN)_2 + Zn \rightarrow K_2Zn(CN)_4 + 2Au.$$

The precipitated gold is treated with dilute sulphuric acid to remove any admixed zinc, after which it is melted with lead and cupelled.



By courtesy of the Ontario Dept. of Mines.

Pouring gold at the Lake Shore Mine.

The mould is resting on a conical slag pot. Bars or ingots of base bullion poured at the mines average 80 pounds in weight and are worth about $20,000 each. At the Ottawa mint, after final refining, gold is poured into ingots worth $10,000 each and weighing 37 pounds avoirdupois; the cubical contents being about equal to an ordinary building brick.

Gold is often refined by electrolysis, using a hot solution of auric chloride ($AuCl_3$) made strongly acid with hydrochloric acid, and containing a little sulphuric acid to precipitate the lead as sulphate. The silver is deposited in the slime as silver chloride.

At the Ottawa Mint, the gold is refined by passing chlorine through the molten metal, which is covered with borax. The silver is removed as silver chloride and floats to the top.

Properties.—Gold is a bright yellow metal of density 19·4. Though harder than lead, it is much too soft to be used in a pure state, and so is alloyed with copper or silver. The purity of gold is generally expressed in " carats ", equivalent to twenty-fourths. Thus the British sovereign is 22-carat, *i.e.* 22/24ths of it is pure gold.

Gold is easily the most malleable and ductile of all the metals. Ordinary gold leaf is 0·0001 mm. thick,—1000 such leaves, pressed together would be about as thick as one leaf of this book. Its extreme ductility is shown by the fact that it can be drawn out to a wire having a thickness of only 1/5000th inch.

It is not attacked by oxygen or water, nor by any single acid with the exception of selenic. Chlorine turns it into auric chloride $AuCl_3$ (soluble), and hence gold will dissolve in aqua regia, a mixture of hydrochloric and nitric acids which yields chlorine. Its reaction with potassium cyanide, and the fact that it forms an amalgam with mercury, have already been considered in connection with the extraction of the metal.

Historical Note.—Owing to the fact that it is found in the free condition, sometimes in the form of nuggets, gold has probably been longer known to man than any other metal. Gold armlets and other ornaments have been found among relics of the New Stone Age, and gold leaf is found in connection with the mummies of ancient Egypt. From very early times it has been woven into ornamental fabrics, *e.g.* "And he made the ephod of gold, blue and purple and scarlet, and fine twined linen. And they did beat the gold into thin plates, and cut it into wires [strips], to work it in the blue, and in the purple, and in the scarlet, and in the fine linen, with cunning work." *Exodus, XXXIX, 2, 3.*

Platinum

Platinum, usually alloyed with small quantities of other " transitional elements ", ruthenium, rhodium, palladium, osmium and iridium (Periodic Table, pp. 68, 69) was found in Columbia (S. America) and later in the Ural mountains, which is now the chief source of the world's supply. Canada ranks third as a producing country. Most of her platinum is obtained from the electrolytic residues which remain after treating the nickel-copper-sulphide ores of the Sudbury district, but in the Rocky Mountain chain (*e.g.* in British Columbia), it is found in placer deposits along with alluvial gold, and is obtained by washing the sands and gravels (*cf.* " panning " for gold). It is then separated from the associated metals by chemical methods which need not be discussed here.

Properties.—Platinum is a silvery-grey metal, probably regarded originally as an inferior kind of silver, for the word is derived from *platina,* a diminutive of the Spanish *plata* (silver). It has a density of 21·4 and melts at 1755°. It is very malleable and ductile, and at a bright red heat can easily be welded. Its coefficient of expansion is about the same as that of glass, and so in the laboratory platinum wire is easily fused into a glass holder. Formerly it was used for sealing into electric lamp bulbs, but cheaper substitutes are now employed (*e.g. manganin,* an alloy of copper, manganese, and nickel).

Platinum resembles gold in its resistance to the chemical action of air and water, and of acids (except aqua regia). This property combined with a high melting point makes it a very suitable material for crucibles; for the same reasons platinum wire and foil are much used in the laboratory,—and would be used far more if the metal were cheaper.

Platinum finds many uses as a catalyst. We have met with it, for instance, in the "Contact process" (when studying the manufacture of sulphuric acid) and it is also much used in the catalytic oxidation of ammonia to nitric acid. One form of " gas-lighter " consists essentially

of a very thin platinum wire. When held in the gas this quickly becomes red hot and so causes it to light. Whatever may be the full explanation, it is certain that it is the *surface layer* of the platinum which stimulates chemical action in such cases, and so the effectiveness of platinum as a catalyst is greatly increased by making it present the largest possible surface. *Platinum sponge, platinum black,* and *platinized asbestos* all consist of platinum so prepared as to secure this result. Platinized asbestos, for instance, is made by soaking asbestos fibres in an alcoholic solution of platinic chloride ($PtCl_4$) and then heating strongly. This decomposes the chloride and a deposit of platinum remains, distributed throughout the asbestos.

Compounds of Platinum.—Of the compounds of platinum which (comparatively speaking) are by no means numerous, we must notice chloroplatinic acid, H_2PtCl_6, which may be prepared in solution by dissolving platinum in aqua regia. Under the (incorrect) name of platinic chloride it is used in analysis as a reagent for potassium compounds, with which it gives a fine yellow crystalline precipitate of potassium chloroplatinate, *e.g.*—

$$H_2PtCl_6 + K_2SO_4 \rightarrow H_2SO_4 + K_2PtCl_6.$$

Questions

1. Mention one physical and two chemical methods by which you could distinguish between a gold chain and a brass one.

2. One method of extracting gold from auriferous quartz consists of crushing the latter, agitating with water and then treating with chlorine, when the gold passes into solution as auric chloride, $AuCl_3$. How do you think the gold could be recovered from this solution?

3. What points of resemblance have you noticed between the (*a*) physical, (*b*) chemical properties of gold and platinum?

4. What is the least quantity of zinc that would be required to displace 20 kg. of gold present in solution as potassium aurocyanide?

5. 5 gm. of auric chloride was completely decomposed by heating to 300° and the weight of gold left was 3·245 gm. The specific heat of gold is ·031. Calculate its atomic weight.

CHAPTER XX

MANGANESE AND CHROMIUM

MANGANESE is not found free in nature. The chief mineral containing it is *pyrolusite,* MnO_2, mostly obtained from Russia. There are deposits in Canada, but they are not very much worked. From pyrolusite, the metal may be obtained by reduction with carbon.

Manganese is a greyish-white metal with a slightly red tinge, and shows a considerable resemblance to iron. Its specific gravity is 7·5 and it melts at 1245°C. The pure metal is comparatively soft, but the presence of small quantities of carbon makes it so hard that it will cut glass, and hardened steel.

It decomposes water even in the cold, hydrogen being evolved, and it dissolves readily in dilute acids giving manganous salts, e.g. with sulphuric acid we have—

$$Mn + H_2SO_4 \rightarrow MnSO_4 + H_2.$$

Manganese forms some important alloys. *Manganin* (Cu, 83 parts; Mn, 13; and Ni, 4) is used for resistance coils, because, after suitable treatment, its electrical resistance scarcely varies with change of temperature. Another use was mentioned on p. 228. *Manganese bronze* (copper, zinc, and a little manganese) is tougher than ordinary bronze and is fairly resistant to the action of sea-water. It is therefore used for making the propellors of steamships.

But the most important alloys of manganese are those with iron. *Manganese steel* consists of iron alloyed with about 12 per cent. of manganese,—some account of it has already been given on p. 185. It is remarkable for the

fact that although it is so hard that it can be used for the jaws of rock-crushers, etc., yet it is not brittle,—it is in fact very ductile.

In working manganese steel, its good qualities prove to be a real embarrassment, for it is so tough that to plane or drill it, a blowpipe or grind stone has to be used.

Spiegeleisen (iron-manganese-carbon) is used in the manufacture of steel as a convenient medium for adding the correct amount of carbon. For the most part, ordinary steel is improved by the presence of *small* quantities of manganese (0·4 per cent. or so), usually introduced as spiegeleisen or as an alloy known as *ferro-manganese.* In fact, the chief use of manganese is in connection with the manufacture of steel.

Oxides.—Manganese forms five oxides. The lowest (manganous oxide, MnO) is a *strong* base, forming well-defined salts such as manganous sulphate, $MnSO_4$. The next (Mn_2O_3) is a *weak* base, and the next (manganese dioxide, MnO_2) is amphoteric (p. 172). After this we have oxides of formulae MnO_3 and Mn_2O_7 which are *acidic.* Most of these oxides are not very important and (except the dioxide) we shall not study them at all. The list has been given, however, in order to bring out one curious and rather general point, *i.e.* that *higher oxides of a given element tend to be more acidic (or less basic) than lower ones.* Examples are fairly numerous. Sulphur trioxide, SO_3, is much more strongly acidic than the dioxide. The two lowest oxides of nitrogen (N_2O and NO) are not acidic at all; the three highest ones (N_2O_3, NO_2, and N_2O_5) certainly are, N_2O_5 being the anhydride of a very strong acid (nitric).

We must now consider in some little detail two compounds of manganese,—the dioxide, MnO_2, and potassium permanganate, $KMnO_4$.

Manganese Dioxide, MnO_2, as already mentioned, is the compound of manganese which occurs most frequently in

nature. Its amphoteric character is evident from the facts that (*a*) with strong bases it can form salts called *manganites, e.g.* calcium manganite, $CaO . MnO_2$, and (*b*) it is possible to prepare a manganese disulphate, $Mn(SO_4)_2$ *i.e.* $MnO_2 . 2SO_3$.

You will already have learned that manganese dioxide is used in the laboratory in connection with the preparation of oxygen and of chlorine. It has important industrial uses. In the Lechanché cell and in "dry cells", it is used as a *depolarizer, i.e.* it oxidizes (to water) the hydrogen which would otherwise accumulate on the carbon plate and prevent the working of the cell. Then it is much used for preventing the green colour which glass tends to have. This colour is due to the presence of ferrous silicate, formed by the action of oxide of iron (present as impurity) upon the silica. The manganese dioxide (*a*) oxidizes this to ferric silicate (yellow) and (*b*) forms a little manganese silicate (violet) on its own account. The violet corrects the yellow giving a colourless product, much as " washing blue " corrects the yellowish tint that washed fabrics tend to show.

Potassium Permanganate, $KMnO_4$.—This consists of purplish-black crystals giving a solution of rich purple colour. In the presence of sulphuric acid *and of a reducing agent to take up the liberated oxygen,* potassium permanganate reacts according to the equation—

$$2KMnO_4 + 3H_2SO_4 \rightarrow K_2SO_4 + 2MnSO_4 + 3H_2O + [5O].$$

The " 5O " has been put in brackets to indicate that it is not actually liberated, but is available for reacting with the reducing agent. Suppose, for instance, the reducing agent were oxalic acid, $H_2C_2O_4$. We may think of this as H_2O+CO_2+CO, and in the presence of sulphuric acid the last member (CO) is converted by the potassium permanganate into CO_2.

As the reaction proceeds, the purple colour of the permanganate is discharged (a practically colourless solution of manganous sulphate being produced). It is therefore very easy to observe the *rate* at which the reaction is proceeding, and in fact this reaction serves as the basis of some very effective experiments showing how the rate of chemical action is affected by (i) the presence of a catalyst, and (ii) temperature.

Effect of Catalyst.—Prepare a solution of potassium permanganate of strength about 3 gm. per litre, and one of crystallized oxalic acid about 6 gm. per litre. Put the permanganate solution into a burette, and put 25 c.c. of the oxalic acid solution into an evaporating dish. Add to it about an equal volume of dilute sulphuric acid, and heat the mixture of the two acids to about 60°C. Now *quickly* run 5 c.c. of the permanganate solution into the oxalic acid solution, and then stir. There is a perceptible interval (about 5 seconds) before the permanganate is decolorized, *i.e.* before it has lost all its "available oxygen" to the oxalic acid.

Heat the contents of the dish once more to 60°C., quickly run in another 5 c.c. of permanganate and stir. This time the action is over in a second or two, in spite of the fact that there is not as much oxalic acid present as there was before, to take up the oxygen.

The reason is that during the first rather slow action, manganous sulphate ($MnSO_4$) was formed in the solution, according to the equation already given. On the second occasion this manganous sulphate acted as a catalyst, and the oxidation of the oxalic acid took place much more rapidly.

To illustrate the effect of temperature, take three beakers, each containing 25 c.c. of the oxalic acid solution to which sulphuric acid has been added, together with 10 c.c. of the permanganate solution (so as to introduce a suitable amount of the manganous salt to act as catalyst). Heat the first mixture to 60°C., quickly run in another 10 c.c. of the permanganate solution, and see how long it takes for this to be decolorized. The second mixture is heated to 40°C. and similarly treated, while the third is dealt with at room temperature. The fact that chemical action takes place more rapidly with increased temperature is very marked (*cf.* q. 6 on p. 236).

Owing to its oxidizing power, potassium permanganate is sometimes used as a disinfectant. It destroys the organic matter by attacking the carbon and hydrogen contained in it, turning these into carbon dioxide and water. In the absence of acid, the permanganate would be reduced to

brown oxides of manganese. A dilute solution of permanganate is for the same reason sometimes used as a throat-gargle,—the doctors tell us that the surface of a sore throat contains organic matter which is serving as food to a swarm of germs.

Chromium

Chromium is a metal which never occurs free in nature. The commonest chromium ore is *chromite* or *chrome-ironstone,* which is really ferrous chromite, $FeO . Cr_2O_3$ or $Fe(CrO_2)_2$. Canada has considerable deposits, but these have not been worked since 1923.

By a series of processes into which we shall not now enter, chromic oxide (Cr_2O_3) may be prepared from chromite, and from this metallic chromium may be obtained by the Thermit process.

$$2Al + Cr_2O_3 \rightarrow Al_2O_3 + 2Cr.$$

This process is exactly as described on p. 169, except that chromium oxide is substituted for ferric oxide.

Chromium is a hard, silver-white metal with a bluish tinge. Its melting point is 1920° and its specific gravity is 6·74. A few years ago it was rarely seen, but it is now commonly met with as the plating on the radiators of automobiles, bath taps, etc. The plating is obtained by electrolysis, using a bath of chromic acid. Many technical difficulties have had to be overcome, and even now there are many problems awaiting solution.

Much chromium is also being used in the manufacture of *stainless steel,* which often contains about 13 per cent. of chromium. *Chrome steel* and *chrome-tungsten steel* are other important products containing chromium, but they have already been described on p. 186.

Oxides of Chromium.—Chromium forms three oxides having the formulae, CrO, Cr_2O_3, and CrO_3, respectively. It is interesting to notice that the first is basic, the second usually basic but may be acidic (as in ferrous chromite, $FeO . Cr_2O_3$), and the third definitely acidic as in potassium

chromate, K_2CrO_4 ($= K_2O \,.\, CrO_3$). This tendency of the oxides to become increasingly acidic with an increasing proportion of oxygen, is, of course, quite in line with what we discussed in connection with the oxides of manganese.

Potassium Chromate, K_2CrO_4, is a yellow, crystalline substance easily soluble in water. We have already noticed its use in testing for lead ion (p. 221). On this reaction is based a process for imparting a permanent yellow dye to textile goods. The fabric is first boiled in a solution of lead acetate. It is then soaked in a boiling solution of potassium chromate, with the result that insoluble lead chromate is precipitated within the fibres of the fabric.

$$Pb\overline{A}_2 + K_2CrO_4 \rightarrow 2K\overline{A} + PbCrO_4.^*$$

Silver chromate is an insoluble dark red substance. Hence potassium chromate may be used in testing for silver.

$$K_2CrO_4 + 2AgNO_3 \rightarrow 2KNO_3 + Ag_2CrO_4.$$

Potassium Dichromate, $K_2Cr_2O_7$.—We may write potassium chromate as $K_2O \,.\, CrO_3$ and potassium dichromate as $K_2O \,.\, 2CrO_3$. Thus we see the point of the prefix " di- ".

Potassium dichromate consists of reddish crystals, less soluble in water than the corresponding chromate. On adding caustic potash the solution becomes lemon-yellow, owing to the formation of the chromate—

$$K_2Cr_2O_7 + 2KOH \rightarrow 2K_2CrO_4 + H_2O.$$

In the presence of sulphuric acid and of a reducing agent, potassium dichromate acts as an oxidizing agent, being itself reduced to the green salt chromium sulphate, $Cr_2(SO_4)_3$. Thus in the dichromate battery, it oxidizes the hydrogen that would otherwise be deposited on the carbon (*cf.* the function of the manganese dioxide in a

* Acetic acid is really $H \,.\, C_2H_3O_2$, potassium acetate $K \,.\, C_2H_3O_2$, and lead acetate $Pb(C_2H_3O_2)_2$, but these formulae may conveniently be written as $H\overline{A}$, $K\overline{A}$, and $Pb\overline{A}_2$.

Leclanché cell). In this case, the sulphates of potassium and chromium ultimately give rise to *chrome alum,*

$$K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O,$$

which is deposited as plum-coloured crystals.

Chromates and dichromates are used (as already indicated) in dyeing, and in preparing insoluble pigments such as *chrome yellow* (lead chromate).

Questions

1. An average specimen of Canadian chromite contains 42 per cent. of chromic oxide (Cr_2O_3). What weight of potassium dichromate could be prepared from 10 tons of the chromite, assuming that there was no waste?

2. One meets with articles made of copper, lead, etc. Why are they never made of manganese?

3. "Higher oxides of a given element tend to be more acidic (or less basic) than lower ones." Consider this principle with respect to (*a*) the two common oxides of carbon, (*b*) stannous oxide and stannic oxide.

4. Glass manufacturers on adding manganese dioxide have sometimes obtained a violet product. How do you account for it? Can you suggest a remedy?

5. A solution of potassium permanganate is sometimes used as a cheap *brown* stain for new wood. How do you account for the brown colour?

6. The following results were obtained in the experiment described on p. 233 ("Effect of Heat"):

Temperature (°C.)	15	20	30	40	50	60
Time (seconds)	60	39	22	15	10	7

   Express them by means of a graph.

7. What weight of potassium permanganate would be required to oxidize 13·9 gm. of crystallized ferrous sulphate, $FeSO_4 . 7H_2O$?

8. We speak of potassium bisulphate and bicarbonate, but it is incorrect to use the term potassium bichromate. Why?

CHAPTER XXI

SOME IMPORTANT HYDROCARBONS

A HYDROCARBON is a compound containing hydrogen and carbon *only*. Do not confuse the word with "carbohydrate". "Hydrate" suggests water, and a carbohydrate is a compound containing carbon, hydrogen *and oxygen*, the last two elements being present in the same proportions as in water. Cane sugar, $C_{12}H_{22}O_{11}$, is an example. Hydrocarbons are sometimes called carbohydrides.

The hydrocarbons are extremely numerous and important, but in this chapter we shall study only three of them, namely, methane (CH_4), ethylene (C_2H_4), and acetylene (C_2H_2).

Methane, CH_4, is sometimes called *marsh gas* because it is formed in marshy pools by the decay of grass, leaves and other organic matter. It is also the chief constituent of the *fire-damp* which has been the cause of so many terrible mine explosions. Manufactured coal-gas contains roughly 30 per cent. of methane, while natural gas often contains 90 per cent. and even more. Natural gas is so extremely abundant in certain parts of Canada that we certainly ought to know something about the properties of its chief constituent.

Preparation.—Methane may be prepared in the laboratory by heating a mixture of sodium acetate (p. 174) and soda-lime in a hard glass flask or, much better, in a copper one. (Soda-lime is made by slaking quick-lime with a strong solution of caustic soda instead of with water). The gas is collected over water—

$$\underset{\textit{Sodium acetate}}{CH_3\,.\,\boxed{COONa + NaO}H} \rightarrow Na_2CO_3 + CH_4.$$

Properties.—Methane is without colour or smell, and is only sparingly soluble in water. It is comparatively difficult to liquefy, having a critical temperature of —83°C. and a critical pressure of 45·6 atmospheres, *i.e.* the temperature must be lowered *at least* to —83°C. before the gas can be liquefied, and at that temperature the pressure required would be 45·6 atmospheres (*cf.* question 1 at the end of this chapter).

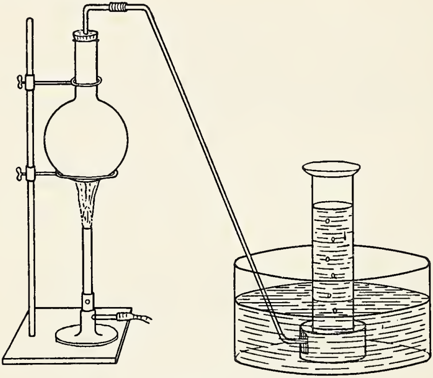


Fig. 35.—Preparation of Methane.

Heat decomposes the gas into carbon and hydrogen, the decomposition becoming rapid at about 1000°C. By carefully controlling the conditions so that decomposition is not carried to completion, considerable quantities of ethylene, C_2H_4, are obtained. As we shall see in the next chapter, the facts just mentioned are of great importance in connection with the industrial utilization of natural gas.

Methane burns in air or oxygen with a slightly luminous flame—

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O.$$

Incidentally, we may notice that if the supply of oxygen is sufficient, *all* hydrocarbons yield the same substances on burning.

As every miner knows, methane and air form a very explosive mixture. The ignition temperature is somewhat high,—in the neighbourhood of 700°C. (*i.e.* rather bright red heat; iron just begins to show dull red at 525°C). This point has a close bearing on the action of the Davy lamp.

Since both carbon and hydrogen combine readily with oxygen, we should expect methane to be a reducing agent, and in the laboratory it is often used for reducing oxides such as those of copper and lead. When we remember that metallic oxides (*e.g.*, Fe_2O_3) are often found in nature or may readily be produced by roasting (*e.g.* zinc oxide is produced by roasting the naturally occurring sulphide), we can see that there may be a great future for natural gas in smelting operations.

If a jar of methane is placed in contact with one of chlorine, a reaction soon takes place with the production of *methyl chloride* and hydrogen chloride—

$$CH_4 + Cl_2 \rightarrow CH_3Cl + HCl.$$

This substitution of chlorine for hydrogen may go further, giving compounds having the formulae CH_2Cl_2, $CHCl_3$ (the well-known *chloroform*), and CCl_4.

Notice that the carbon atom in methane cannot "add on" chlorine,—it can only take on atoms of chlorine by shedding an equal number of hydrogen atoms. The fact is that the carbon atom has only four valency bonds (we think of it as $-\overset{|}{\underset{|}{C}}-$), and when these are all engaged no more atoms can be attached. Compounds such as methane, in which the valency bonds are all engaged, are said to be *saturated* and are said to give rise to *substitution products* (*e.g.* chloroform).

Starting from methane, CH_4, we have a whole series, —ethane (C_2H_6), propane (C_3H_8), butane (C_4H_{10}), and so on—each differing in formula from the preceding one by the addition of CH_2. It is not very obvious at first

that in all these the carbon atom is tetravalent, but we may write

$$C_2H_6 \text{ as } \begin{array}{c} \\ \\ H - \end{array}\!\!\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{c} \\ \\ - \end{array}\!\!\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{c} \\ \\ - H, \end{array} \quad C_3H_8 \text{ as } \begin{array}{c} \\ \\ H - \end{array}\!\!\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{c} \\ \\ - \end{array}\!\!\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{c} \\ \\ - \end{array}\!\!\begin{array}{c} H \\ | \\ C \\ | \\ H \end{array}\!\!\begin{array}{c} \\ \\ - H \end{array}$$

and so on, some of the valency bonds of the carbon atoms being exercised on other carbon atoms. Thus, the members of the series are all saturated compounds.

Further, they closely resemble one another in other chemical properties, and indeed they are usually distinguished from one another *not* by their chemical properties but by physical ones, such as density, melting point, boiling point, etc. Notice that the series can be expressed by the general formula C_nH_{2n+2}; *e.g.* if $n = 1$, we have CH_4, if $n = 2$, we have C_2H_6, and so on. It is known as the *paraffin series* because the higher members, from about $C_{17}H_{36}$ upwards, are present in ordinary paraffin wax (Lat. *parum affinis* = slight affinity). The latter is so called because it was found to be very resistant to acids, alkalies and indeed most chemical reagents.

A series of compounds such as we have discussed is known as a ***homologous series***, which may be defined as *a series of compounds which have similar chemical properties and whose formulae are all included in a single general expression.* In organic chemistry (*i.e.* the chemistry of the compounds of carbon) there are many examples of homologous series.

Ethylene, C_2H_4, is usually prepared in the laboratory by heating ordinary alcohol, C_2H_5OH, with sulphuric acid. At first sight it looks as though the action of the sulphuric acid was simply to withdraw the elements of water ($C_2H_5OH - H_2O = C_2H_4$). The change is not really as simple as this, but we need not discuss it here. As already mentioned, a certain amount of ethylene is produced when methane is heated under suitable conditions out of contact with air.

Unlike methane, ethylene is capable of forming *addition compounds* with chlorine, bromine, etc. Thus, in contact with bromine vapour, oily-looking drops of ethylene dibromide, $C_2H_4Br_2$, are formed. It was because of this reaction that ethylene was formerly known as *olefiant gas* (Lat. *oleum* = oil, *fieri* = to become). Owing to its property of forming addition compounds, ethylene is said to be an *unsaturated* hydrocarbon, and its "structural formula" is written as

$$\begin{array}{ccccc} H & & & & H \\ & \diagdown & & \diagup & \\ & C & = & C. & \\ & \diagup & & \diagdown & \\ H & & & & H \end{array}$$

The formula suggests that the carbon atoms are still tetravalent, but that each of them has one of its valency bonds in reserve, so to speak. On combining with bromine the "double bond" becomes a single one, and the compound would be expressed by the formula

$$\begin{array}{ccccccccc} & & H & & & & H & & \\ & & & \diagdown & & \diagup & & & \\ Br & - & & C & - & C & & - & Br. \\ & & & \diagup & & \diagdown & & & \\ & & H & & & & H & & \end{array}$$

We should rather expect that ethylene would also be capable of combining with *hydrogen*, forming the saturated compound ethane, C_2H_6. The action readily takes place when a mixture of the two gases is passed over finely-divided nickel at about 140°C. This addition of hydrogen to an unsaturated compound has received a very important application in the conversion of cheap oils into valuable fats. There is some reference to it on p. 3 of the Introduction.

Ethylene is the lowest member of another homologous series called the *olefine* series, the next members being propylene, C_3H_6, butylene, C_4H_8, pentylene, C_5H_{10}, and so on. The general formula in this case is C_nH_{2n}.

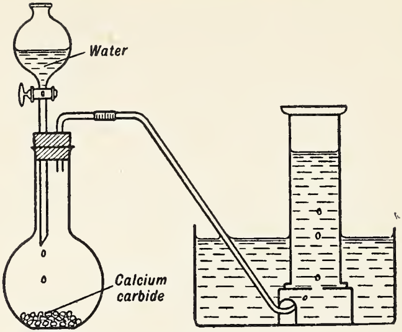


FIG. 36.—Preparation of Acetylene.

Acetylene, C_2H_2.—The "acetylene lamp" reminds us that the ordinary way of preparing this gas is by the action of water on calcium carbide—

$$CaC_2 + 2H_2O = Ca(OH)_2 + C_2H_2.$$

(N.B.—A very common error is to write $CaC_2 + H_2O = CaO + C_2H_2$; but CaO is the formula for quick-lime, and this could not exist in the presence of water.)

To collect a few jars of the gas in the laboratory, we may conveniently use the apparatus indicated in Fig. 36.

Acetylene is colourless, and when pure has a not-unpleasant smell. The "carbide" smell usually associated with it is really due to the presence of impurities. It is slightly soluble in water.

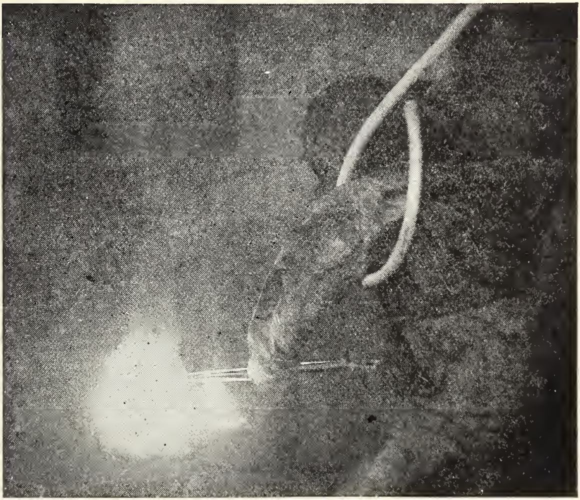
Its structural formula includes a "triple bond", $H - C \equiv C - H$, indicating that the compound is highly unsaturated, each carbon atom having two valency bonds in reserve. Thus, acetylene readily forms addition compounds having such formulae as

$$\begin{array}{ccccc} Cl & & & & Cl \\ & \diagdown & & \diagup & \\ & & C = C & & \\ & \diagup & & \diagdown & \\ H & & & & H \end{array} \quad \text{and} \quad \begin{array}{ccccccc} & & Cl & & Cl & & \\ & & & \diagdown \quad \diagup & & & \\ H & - & C & - & C & - & H. \\ & & & \diagup \quad \diagdown & & & \\ & & Cl & & Cl & & \end{array}$$

We have already seen that methane is the lowest member of a homologous series of general formula C_nH_{2n+2}, and ethylene of another one of general formula C_nH_{2n}. There is also a homologous series of general formula C_nH_{2n-2}, acetylene being the lowest member of it. All the members of this series, like acetylene itself, are highly unsaturated.

When heated to about 550°C. acetylene undergoes a curious change known as *polymerization,* several molecules joining together to form a more complex one. The product is a liquid containing a number of substances, among which the well-known compound *benzene,* C_6H_6, has been recognized.

Acetylene burns with an extremely bright, but very smoky flame, indicating that combustion is not complete.



By courtesy of Messrs. Siebe, Gorman & Co., Ltd. (Diving Engineers).

Diver working on a wreck with oxy-acetylene flame, 38 feet below the surface.

This is not surprising when we consider the equation $2C_2H_2 + 5O_2 = 4CO_2 + 2H_2O$, which shows that for the complete combustion of one volume of acetylene, $2\frac{1}{2}$ volumes of oxygen would be required, *i.e.* $12\frac{1}{2}$ volumes of air, since only about one-fifth of the air consists of oxygen.

In the employment of acetylene as an illuminant, the burners first used gave unsatisfactory results because they failed to supply a sufficient volume of air, with the result that much free carbon was produced. The difficulty has been overcome by the use of a burner in which the gas issues through two (or more) very fine jets, arranged so as to suck in air somewhat on the principle of the bunsen burner.

A flame of acetylene fed with oxygen has an extremely high temperature, and is much used for cutting and welding. Most varied work can be undertaken, as will be seen from the illustration, which shows a diver using the flame for cutting steel under water. Some time ago the entire after-part of a large ship was cut off, just as one might cut through a toy boat with a saw.

The high temperature of the flame is partly due to the fact that acetylene is an *endothermic* compound, *i.e.* when it is formed from its elements heat is absorbed, and therefore when it is decomposed an equal amount of heat is given out. We can divide the burning of acetylene into two stages,—(i) decomposition, (ii) oxidation of the carbon and hydrogen produced in (i). During *each* of these processes heat is given out. Most compounds are exothermic, and if they are burned, heat is *absorbed* during the decomposition part of the process.

As acetylene is used to such a large extent in industry, the question of storage is an important one. At one time the method universally adopted was to supply it in cylinders under high pressure (*cf.* oxygen). It was found, however, that under certain circumstances disastrous explosions resulted, and in some countries (*e.g.* England) it is now illegal to supply the gas in this form. Instead, use is made of the fact that acetylene is very soluble in a liquid called ace-

tone, the solubility being proportional to the pressure in accordance with what is called Henry's Law. As the pressure is released, the acetylene escapes, much as carbon dioxide escapes from a freshly-opened bottle of mineral water. However, many works have eliminated the problem of storage altogether by generating their gas as they need it, from water and calcium carbide.

Questions

N.B.—See note in italics, p. 20.

1. The question of the cheap transportation of methane, from the natural gas districts in which it occurs to the large towns, is obviously an important one. What do you think of the suggestion that it should be liquefied, and then conveyed in strong metal cylinders?

2. What volume of air, assumed to contain one-fifth of its volume of oxygen, would be required for the complete combustion of one cubic foot of methane?

3. A certain gaseous hydrocarbon is found to contain 82·8 per cent. of carbon. At 21°C. and 75 cm. pressure, 1 litre of it weighs 2·39 gm. Find (i) its simplest formula, (ii) its molecular formula.

4. "The ignition temperature [of methane] is somewhat high. . . . This point has a close bearing on the action of the Davy lamp." p. 239). Explain the connection.

5. Write the structural formula for pentane, C_5H_{10}.

6. How do you account for the fact that acetylene burns with a more luminous flame than ethylene, and ethylene than methane?

7. How many cubic feet of acetylene, measured at N.T.P., would be obtained by the action of water on 1 lb. of pure calcium carbide? (1 lb. = 454 gm. and 1 cu. ft. = 28·3 litres.) How many grams of calcium hydroxide would be produced?

8. It was found that 12 c.c. of a certain gaseous hydrocarbon required 24 c.c. of oxygen for complete combustion, and that 12 c.c. of carbon dioxide was produced.
   What is the compound? How would you prepare a few jars of it in the laboratory?

CHAPTER XXII

NATURAL OIL, GAS, and TAR

There is no doubt that man has been interested in natural oil and gas from very ancient times, and that to at least a small extent he has made use of them. Pliny, for instance, writing in the first century A.D., mentions the use of oil for illumination in Agrigentum (Sicily), and students of the ancient literatures of China and Japan tell us that these contain many references to the use of natural gas for lighting and heating. Further, people have often speculated as to the origin of those ancient religions in which the worship of fire is the central feature. It is reasonably suggested that at least some of them may have grown up among tribes who lived in gas and oil regions, and had been awed by the spectacle of flames and smoke on a gigantic scale, evoked perhaps by a flash of lightning.

During the last half century or so it has been found that petroleum (as oil occurring in the ground is usually called) is very widely distributed. To mention only a few places, it occurs in commercial quantities in the United States and Canada, in Argentina, Russia, Egypt, Persia, and the Dutch East Indies,—in every continent, in fact, except Australia, and it is found even there, but not so far in paying quantities. At present the United States is much the greatest producer. Canada, however, has large supplies which she is now rapidly developing. They are found chiefly in Alberta, which produces about nine-tenths of the Canadian output of oil, and about two-thirds of the output of natural gas.

The latter usually consists of a mixture of the lowest members of the paraffin series (p. 240), methane greatly predominating. Thus, a typical analysis of gas from the Turner valley in Alberta gave methane 89%, ethane (C_2H_6) 5·2%, propane (C_3H_8) 3·7%, and higher hydrocarbons (chiefly paraffins) 2·1%. The results vary a good deal from one district to another. Some specimens, for instance, contain a small amount of helium,—seldom more than 1% —and the Baku gases contain some of the lower olefines; but the analysis given may be regarded as broadly representative.

The oils also, at least those obtained in America, consist mainly of paraffins, of formulae C_5H_{12} (pentane), C_6H_{14}, etc. up to about $C_{15}H_{32}$. They usually contain in solution both the lower members (gases) previously mentioned, and also solids of formulae $C_{16}H_{34}$, $C_{17}H_{36}$ and upwards.

The bitumen found in various parts of the world (notably in Trinidad and in the "tar sands" of Alberta) is certainly closely related to petroleum. As to exactly what compounds are contained in it comparatively little is known, but no doubt higher hydrocarbons (probably paraffins) are present, together with other compounds formed by oxidation.

Having thus glanced at the composition of natural oil, gas, etc., we shall now briefly consider the methods used in obtaining and (where necessary) purifying them.

To obtain oil it is usually necessary to sink a well, and here the first step is to erect a derrick. For a deep well this would be at least 70 feet high, so as to provide room for the manipulation of the boring tool. The latter may consist of a sort of chisel weighing about a ton; or it may work on the gimlet principle, fresh sections being constantly screwed on as the earlier ones disappear into the earth. Among other appliances, there are some for the regular removal of sand and water, and for "fishing", *i.e.* recovering drills, etc. which have accidentally broken off, and which by their presence prevent further progress

in drilling. When fishing operations are unsuccessful, it is sometimes necessary to abandon drilling which may have been in progress for months.

A hole drilled as we have described would readily cave in, but this is prevented by lining it with an iron casing.

If oil is present, it will be contained in a porous rock such as sandstone or limestone, often under great pressure.

By courtesy of Dept. of Lands and Mines, Alberta.

Gas and oil well out of control through faulty engineering.

"Striking oil" can be a very exciting experience. At Lakeview, in California, for instance, oil was encountered at a depth of 2300 feet. It rushed up with such force as to blow off the top of the derrick, and shot up in the air to a height of 300 feet, pouring out oil at the rate of nearly two million gallons a day. The "gusher", however, is the exception rather than the rule, and after sinking the well, it is usually necessary to raise the oil by pumping operations.

The oil obtained is occasionally used in its crude condition, *e.g.* as a fuel for locomotives and steam-boats, but it is usually *refined*. The first step in this process consists in distilling the crude oil, and changing the receiver from time to time as the boiling point rises. Thus, a first

"fraction" might be obtained consisting of carbohydrides which boil at temperatures up to 40°C., a second between 40°C. and 90°C., and so on. We may distinguish broadly between the *naphthas* which distil over at temperatures up to 150° or so, and *kerosene* which comes over at 150°

By courtesy of The Canadian Western Natural Gas, Light, Heat & Power Co., Ltd.

Flame at Home Well No. 1, Turner Valley Field, Alberta.

to 300°. The naphthas of lower boiling point (40° to 90°) give us *gasoline,* while the higher ones are used as solvents for resins, rubber, etc. Among the latter is *benzine* (not to be confused with *benzene,* C_6H_6), much used in dry-cleaning because of its power of dissolving grease.

After the kerosene has distilled off, the liquid remaining in the still is allowed to cool. This causes the solid substances present in solution to separate out, ordinary solid *paraffin* being thus obtained. This is removed by means of a filter press, and from the viscid liquid which filters through, *lubricating oils* and the familiar *vaseline* are obtained.

At the present time the demand for gasoline is much greater than that for kerosene, *i.e.* the hydrocarbons of lower boiling point are preferred. Now, low boiling point goes with low molecular weight and vice versa, *e.g.* hexane, C_6H_{14}, boils at 69°C., decane, $C_{10}H_{22}$, at 173°C., and tetradecane, $C_{14}H_{30}$, at 252°C. Hence, steps are taken to break up the molecules of these higher hydrocarbons. This may be done by increasing the pressure in the still and then distilling them at a temperature above their normal boiling points. In this way the higher *paraffins* (general formula C_nH_{2n+2},—*cf.* p. 240) are broken up into a mixture of lower paraffins and *olefines* (general formula C_nH_{2n}), *e.g.* from $C_{18}H_{38}$ we might obtain $C_5H_{12}+C_{13}H_{26}$, or $C_6H_{14}+C_{12}H_{24}$, —with many other possibilities. The chemical change is known as *cracking*. Associated with petroleum there is often natural gas. This also is contained under high pressure in the porous rock,— quite commonly 200 to 300 lb. per square inch and sometimes as much as 1000 lb. It is led away in very wide pipes and finally reaches the consumer through narrow ones, and with its pressure reduced to about 4 oz. per square inch. Both for domestic and industrial purposes, natural gas is very widely used in Canada and the United States.

Natural gas is often "wet", *i.e.* it contains the vapour of liquid hydrocarbons, especially those of low boiling point. A famous example is the gas obtained from the Turner valley in Alberta. By compressing it, carbohydrides of the valuable naphtha group are readily obtained,—more than 900,000 barrels in the year 1929. The profusion with which the Turner valley field produces gas is, in fact, a real source of embarrassment, for at

present about 90 per cent. of it is wasted. In June of 1930 the wastage was something like 560,000,000 cubic feet per day,—probably ten times the weight of the oil secured,—and simply considered as fuel this has been calculated as equivalent to dumping 25,000 tons of coal daily into the ocean.

Something like 4,000,000 cubic feet per day are now being salvaged by storing the gas in the partially depleted gas sands at Bow Island, but obviously this only touches the fringe of a very serious problem.

However, it has long been obvious to the chemist that natural gas might be utilized in many other ways than simply as a fuel or as a source of light. When these alternatives have been properly developed the problem of gas wastage will disappear, so it is worth while to consider some of them.

First, there is no doubt that natural gas might be used for the reduction of ores for which at present coal and coke are chiefly employed. Experiment shows that one ton of zinc may be obtained from zinc ore by the use of 12,000 cubic feet of gas instead of one ton of coal. The reduction of iron ores by the use of natural gas has also been suggested.

Another use to which natural gas might be put is the manufacture of *carbon black,* obtained by burning the gas with a supply of air insufficient for complete combustion. The carbon black thus obtained is of very high quality, and there is a great demand for it in the rubber industry, and to a less extent in the ink and paint industries. Certainly the process seems wasteful. 1000 cubic feet of natural gas contains about 34 lb. of carbon, but the highest yield of carbon black so far obtained is only about 1·4 lb.,[1]—and, of course, all the hydrogen is lost. On the other hand, the manufacture could be carried out on the spot, and the product is so valuable that freight charges would be relatively insignificant.

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[1] Higher yields have been obtained by an electric arc method, but the process is too expensive.

Next, we must notice the possibilities of natural gas as a means of generating electric power. 350 million cubic feet per day are used in this way in the United States, and, except for the existing abundance of hydro-electric power, there seems no reason why such a method of disposal should not be used in Canada. The method suggested is to blow the gas through turbines and then burn it under high pressure boilers.

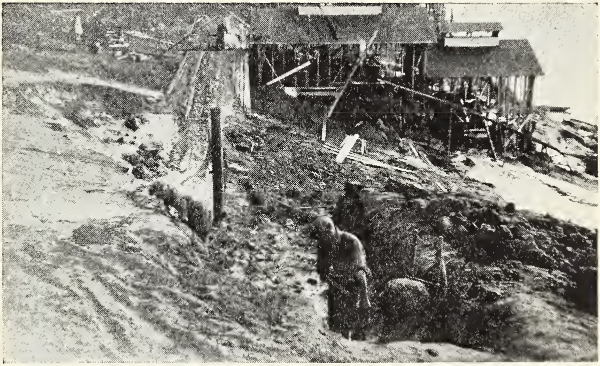
Evidently much can be done with natural gas even in its present form (*i.e.* mainly methane). But methane is a *par-affin,* and, therefore, from the chemist's point of view, a very intractable substance. For this reason he suggests first turning it into ethylene (C_2H_4) and other olefines. There are several methods of effecting this conversion, one of them being the action of heat under properly regulated conditions. With olefines as a starting point the chemist can do a great deal. He can polymerize them into liquid hydrocarbons boiling within the gasoline range of temperature, much as acetylene can be polymerized into benzene (p. 243). Very promising work along these lines is being done by the National Research Council. It has also been found that with the help of aluminium chloride the olefines can be polymerized into heavy lubricating oils.

Most important of all, however, is the possibility of using ethylene as the starting point of a large number of synthetic organic products,—ethyl alcohol, acetic acid, acetone, various esters, etc. At present this starting point is provided by acetylene, prepared from water and calcium carbide; but all the products derived from acetylene could also be obtained by starting from ethylene.

It is very obvious that natural gas is a product full of possibilities. Another substance which provides many problems for the chemist is the bitumen mentioned on p. 247, but it is at any rate free from the embarrassing property of disappearing while one is thinking about it.

The "tar sands" as these bituminous deposits are often called, are situated in the McMurray district of Alberta.

They cover an area of at least 6000 square miles, and probably of more than twice that amount. At first the deposits were regarded merely as a source of paving material, and in 1915, in Edmonton, demonstration pavements were laid down which still show no signs of deterioration after nearly 20 years of heavy traffic. Later it was shown that by comparatively simple distillation methods, 500 lb. of tar of 99·5% purity could be obtained from a ton of one of the better grade samples.



By courtesy of International Bitumen Co., Ltd.

Quarrying bituminous sand. The standpipe represents the casing of a test well.

There is no doubt, however, that by a process of cracking (p. 250) these deposits could be made to yield vast supplies of oil including gasoline. It is probably fair to assume that there are 200,000 tons of bituminous sand per acre, and that a barrel of petroleum could be prepared from two tons of sand. Given the area of the deposits, the student with a fondness for arithmetic can easily work out the rest for himself. At present, oil prepared from these deposits cannot compete in price with the natural product

from the wells. But the time must come when the latter will become scarcer, with a corresponding rise in price,[1] and it may well be that the McMurray deposits will then serve as one of the world's richest sources of supply.

Questions

1. Some time ago a man wrote to a newspaper asking if any reader could kindly supply him with the chemical formula for gasoline. What would be your answer?

2. Suppose the paraffin eicosane ($C_{20}H_{42}$) were "cracked" in such a way as to yield lower paraffins of formulae C_6H_{14} and C_7H_{16}. Give the formulae of the olefines that would be produced at the same time, writing down the equations.

3. If the 560,000,000 cubic feet of gas wasted daily in the Turner valley consisted entirely of methane, and were measured at N.T.P., what would be the weight of gas lost? (1 cubic ft. of hydrogen at N.T.P. weighs 0·00562 lb.).
   Actually the weight lost would be much greater than your calculation indicates. Why?

4. "1000 cubic feet of natural gas contains about 34 lb. of carbon." Check this statement, assuming that the natural gas consists entirely of methane and is measured at N.T.P. (1 cubic ft. of hydrogen at N.T.P. weighs 0·00562 lb.).

5. It has been suggested that the surplus natural gas of Alberta should be used for (i) the reduction of ores, (ii) the generation of electric power, (iii) the production of carbon black. Summarize what seem to you the advantages and disadvantages of each of these methods.

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[1] In some parts of Ontario the price of natural gas has risen during recent years from 30 cents to 80 cents per 1000 cubic feet.

CHAPTER XXIII

STARCH, SUGARS, and CELLULOSE

STARCH, various sugars and cellulose are grouped together in this chapter because in their composition they have one point in common,—they are all ***carbohydrates,*** a term which we shall not be far wrong in defining as *compounds containing carbon and the elements of water.* It follows that the number of hydrogen atoms will be twice that of the oxygen atoms, and can sugar, for instance, has the formula $C_{12}H_{22}O_{11}$.

Avoid saying "compounds of carbon with water". Cane sugar does not contain water though it contains the elements from which water may be made,—just as a large house does not contain a cottage, though it probably contains the bricks, etc., from which a cottage could be made.

Starch

Starch has the formula $(C_6H_{10}O_5)_n$, a point to which we shall return a little later in the present chapter. The substance is found in various parts of plants, especially in seeds (*e.g.* the grains of wheat, corn, etc.) and in tubers (*e.g.* potatoes). It is stored here to serve as food for the young plant, and possesses the great advantage that as starch it is insoluble in cold water and so cannot be washed out, while at the proper time it can readily be turned into sugar so as to be available as food.

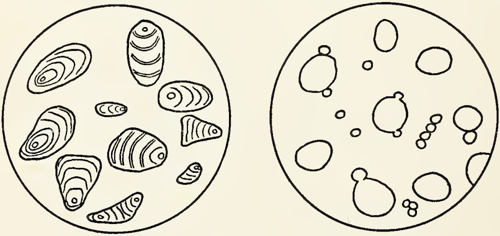
It is obtained in Europe chiefly from rice or potatoes, and in America from corn. The material is first softened and crushed, and then washed through a fine sieve by means of a stream of water. The result is that the starch

granules pass through, while the *gluten* (or vegetable albumin) and cellulose (p. 262) remain behind. This part of the manufacturing process is readily imitated by tying up a handful of flour in a fine muslin bag and kneading it under water. The starch grains pass through giving the water a milky appearance, while the sticky gluten remains behind in the bag.

On a manufacturing scale, the crude starch obtained as above is placed on long sloping wooden troughs and treated with water, so that the lighter fibrous particles may be removed. It is then drained by means of a centrifugal machine and finally dried.

Properties.—Starch consists of minute grains made up of a nucleus surrounded by concentric layers, but the size, shape, and general appearance of these grains depend on the source of the starch. Two varieties are illustrated in Fig. 37.

Starch is insoluble in cold water, but on heating, the granules swell up and burst. The contents of the cells (*granulose*) now pass into solution, the latter on cooling



(*a*) Potato. (*b*) Wheat.

Fig. 37.—Starch granules $\times 250$.

forming the familiar *starch-paste*. The cell-walls themselves, however, (*starch cellulose*) are insoluble, and cause the solution to have a somewhat turbid appearance.

We have said that the granulose dissolves, but this statement probably needs qualification. Most likely what is formed is a *colloidal* solution (*cf.* p. 97), the starch particles present consisting not of single molecules but of

groups of molecules, each group, however, being much too small to be visible under the highest power of any ordinary microscope.

We are now in a position to understand how the formula for starch is arrived at. Analysis indicates that the simplest formula is $C_6H_{10}O_5$ (*cf*. question 1). Working with starch "solution" we can now observe the depression of freezing point as described in Chapter II and calculate the molecular weight. The result obtained is about 32000! This indicates that if starch is $(C_6H_{10}O_5)_n$, n must be about 200. The formula *may* be $C_{1200}H_{2000}O_{1000}$, or the solution may contain groups of molecules, each containing some 200 of the simpler $C_6H_{10}O_5$ molecules or say 100 molecules of formula $C_{12}H_{20}O_{10}$. There are evidently plenty of other possibilities, but at present we have no sure means of deciding between them.

With iodine, starch gives a characteristic blue colour, and the test is so sensitive that 1/250th of a milligram can be detected in this way. Apparently the action is physical rather than chemical, the iodine being adsorbed (p. 173) by the colloidal particles of starch.

If a little extract of malt in water is added to starch paste, and the mixture is kept at a temperature of about 60°C., it soon becomes limpid. Several substances are formed in succession, the final product being a sugar known as *maltose*. The action is due to the presence in the malt extract of a substance called *diastase*. A very similar substance, ptyalin, is present in the saliva. Hence, by chewing, starchy substances are converted into a sugar, —soluble, and therefore much more easily digested.

Sugars

Cane sugar or **sucrose,** $C_{12}H_{22}O_{11}$, is found in the roots and stems of many plants, notably in the root of the beet and the stem of the sugar cane. It is also found in the sap of certain trees, especially the maple.

It has a long history, dating back at least to the time when the ancient Greeks listened to stories of a strange

honey, made without bees, which was somehow obtained from reeds growing in India. Arabs obtained the canes and took them to Spain, whence years later they were conveyed to the West Indies. Here they flourished wonderfully, and for several centuries these islands were the chief source of the world's sugar supplies.

By courtesy of the Imperial Institute, London.
Sugar Maples with sap buckets attached.

In 1747 the German chemist Marggraf showed that the same sugar was also present in beet-root, but it was not till about 1830 that sugar began to be obtained from beet-root on a really large scale. The method of extraction is worth a little notice, and we shall understand it better if we remember that beet-root juice contains in solution (besides sucrose), a number of solid acids (chiefly citric, oxalic, tannic, and tartaric), albumin, and another sugar called raffinose. After the roots have been washed, they are cut into very thin slices by a special machine, and these are then soaked for some time in warm water. The cell walls present in the root act as a separating membrane. Most of the albumin and non-crystalline products remain in the cells, while cane sugar and other crystallizable sub-

stances diffuse through into the warm water. The latter is now heated with lime, the result being that the acids are precipitated in the form of their calcium salts, while any albumin that may be present is coagulated (*cf.* effect of heating white of egg). Further, the lime forms with the cane-sugar a compound known as *calcium saccharosate,* $C_{12}H_{22}O_{11} . CaO$, but this is decomposed by passing carbon dioxide through the solution—

$$C_{12}H_{22}O_{11} . CaO + CO_2 \rightarrow CaCO_3 + C_{12}H_{22}O_{11}.$$

The mixture is now filtered, and the clear juice is evaporated until it begins to crystallize. After cooling, the mother liquor ("molasses") is separated from the crystalline portion by means of a centrifugal extractor.

At this stage, the sugar has a brownish colour and has to be *refined.* For this purpose it is dissolved in water and submitted to several processes, of which the chief consists in passing it through long cylindrical vessels filled with animal charcoal, which adsorbs the colouring matter (*cf.* p. 173). The colourless solution is then once more concentrated by evaporation until it begins to crystallize out.

Properties.—Cane sugar crystallizes in prisms which melt at 160°C., and are easily soluble in water. When heated in a large covered crucible it yields a very pure form of carbon known as *sugar charcoal.* With concentrated sulphuric acid,—especially if a little water is first added,—cane sugar undergoes a very striking change, frothing up and charring, while carbon dioxide and sulphur dioxide are given off. No doubt the sulphuric acid first withdraws the elements of water ($C_{12}H_{22}O_{11} \rightarrow 12C + 11H_2O$), the carbon then reducing the acid to sulphur dioxide and being oxidized itself.

When heated with *dilute* sulphuric acid, cane sugar is converted into two simpler sugars known as *dextrose* and *levulose* (the sulphuric acid acting as a sort of catalytic agent)—

$$C_{12}H_{22}O_{11} + H_2O \rightarrow \underset{\textit{Dextrose}}{C_6H_{12}O_6} + \underset{\textit{Levulose}}{C_6H_{12}O_6}.$$

It seems curious that two different substances should both have the same formula. The fact is that though molecules of dextrose and levulose both contain the same atoms, the atoms are arranged in different ways in the two cases. We can obtain an easy illustration from children's toys. One child might build a "house" with his box of blocks and another child with an exactly similar box might build a quite different house,—the houses would have the same composition, and yet they would not be similar.

The phenomenon we are discussing,—two compounds having the same chemical composition and yet differing in properties,—is known as ***isomerism.*** Dextrose and levulose, for instance, would be described as isomeric compounds, or simply as isomers. The phenomenon is particularly common in connection with the compounds of carbon (though it is not confined ot them), and that is one reason why their number is so enormous.

We shall see in Chapter XXV that dextrose can be fermented with yeast, giving carbon dioxide and alcohol. Cane sugar cannot be *directly* fermented. However, yeast contains a soluble nitrogenous substance known as *invertase,* which turns cane sugar into dextrose and levulose (equation already given). These simpler sugars then undergo fermentation by the yeast.

In one form or another, cane sugar is extensively used as an article of food, and the annual consumption in Canada is 92 lb. per head. It possesses antiseptic properties and so is used in making jam, marmalade, etc. The germs of putrefaction are killed by the boiling process, and the added sugar then forms a medium in which new germs are unable to thrive.

Sugar candy, barley sugar and *caramel* require a brief notice. The first consists of large crystals, and is made by hanging threads in a solution of cane sugar, crystallization then taking place slowly round the threads. Barley sugar is made by heating cane sugar with a little water. After a while it melts (there is too little water present to dissolve much of it). It then begins to turn yellow, and

at this stage it is allowed to cool, giving a hard, glassy-looking mass.

On heating sugar to a temperature somewhat above its melting point, it forms a brown soft substance known as caramel. This is used in confectionery and in tinting brandy, whisky, etc.

Dextrose, $C_6H_{12}O_6$, is also known as *glucose* and as *grape sugar*. It received the last name because it is found in the juice of ripe grapes, and when these have been converted into raisins the little crystals are often observed. Dextrose is also found in other ripe fruits, and in flowers.

On a commercial scale it is manufactured by boiling starch with water to which a little sulphuric acid has been added—

$$(C_6H_{10}O_5)_n + n\,H_2O \rightarrow n.\,C_6H_{12}O_6.$$

Chalk is afterwards added to neutralize the acid and the liquid is filtered, dextrose being obtained on evaporation of the filtrate. Other substances are present, but are not deleterious.

Dextrose can be distinguished from cane sugar by the fact that it reduces silver oxide. A solution of sodium hydroxide is first added to one of silver nitrate, giving a brown precipitate of silver (hydr)oxide. This is then just re-dissolved with dilute ammonia—

$$2NH_4OH + 2AgNO_3 \rightarrow 2NH_4NO_3 + 2AgOH\,(= Ag_2O + H_2O).$$

On adding a little solution of dextrose and gently warming, a silver mirror is obtained (*cf*. p. 206).

Dextrose is largely used as a sweetening material in the manufacture of confectionery, jam, preserved fruits, etc.

Levulose, $C_6H_{12}O_6$, also known as fructose or fruit sugar, is found together with dextrose in many fruits. It is probable that cane sugar is first formed, and that the two simpler sugars are then produced by hydrolysis (equation on p. 259).

Levulose is now being produced commercially for the use of persons suffering from diabetes. Such patients are

unable to assimilate ordinary sugar, but seem able to assimilate levulose.

Lactose or milk-sugar, $C_{12}H_{22}O_{11} . H_2O$ is *not* cane sugar combined with one molecule of water of crystallization. The fact is that (except for the H_2O) milk-sugar and cane sugar are isomers.

Lactose is present in the milk of mammals, and is actually prepared from cow's milk. Rennet is added, and the curds are removed to serve for the preparation of cheese. From the *whey* which is left, lactose may be obtained by evaporation.

Certain bacteria which very readily obtain access to milk have the power of converting lactose into lactic acid, a fact of which we are reminded when milk turns sour.

Cellulose

Cellulose, like starch, has the formula $(C_6H_{10}O_5)_n$, but the resemblance is rather superficial, for n almost certainly has very different values in the two formulae; besides which, of course, we have to reckon with isomerism.

Cellulose forms the framework or skeleton of vegetable tissues, and is therefore one of the principle constituents of *wood.* Nowadays most of the paper we use is prepared from wood, and certain kinds of paper, notably Swedish filter paper, consist of almost pure cellulose. Cotton wool and linen are also very pure forms of this substance. It has been found that the difference between cotton wool and linen is not chiefly chemical, but physical, and is traceable to differences in the structure of the fibres.

Towards most chemical reagents cellulose is really very inert, and this accounts for the fact that almost anything can be filtered through paper. The latter, however, is readily charred by concentrated sulphuric acid (so also is wood, as people soon find when they have spilt this liquid on the laboratory bench). Remembering that sulphuric acid has a strong affinity for the elements of water, you can easily account for the charring.

If sulphuric acid, however, is slightly diluted (by pouring two volumes of the acid into one volume of water) and paper is dipped into it, the paper becomes very tough and translucent. After washing it free from acid and drying it, we have *parchment paper.*

If cellulose in the form of pure cotton wool is treated under suitable conditions with a mixture of nitric and sulphuric acids, cellulose hexanitrate, commonly known as *guncotton,* is produced,—

$$(C_6H_{10}O_5)_2 + 6HNO_3 \rightarrow C_{12}H_{14}O_4(NO_3)_6 + 6H_2O.$$

The action would be reversible, but the sulphuric acid (which, of course, has a strong affinity for water) may be regarded as removing the water as fast as it is formed, and so the reverse action is prevented.

Guncotton still shows the fibrous texture of the original cotton wool, but burns with extreme rapidity. When pressed into cartridges it forms a powerful explosive. A rough comparison between gunpowder and guncotton is instructive. In gunpowder, the oxygen necessary to oxidize the carbon is supplied from an outside molecule, the potassium nitrate (KNO_3). In guncotton, the oxygen and carbon are both contained in the same molecule. They are *closer* to one another, and so we should expect the explosive action to be compressed into a shorter interval of time, as is indeed the case.

Another explosive somewhat closely related to guncotton is *cordite,* made from guncotton and nitro-glycerine $C_3H_5(NO_3)_3$, also a powerful explosive (liquid). The guncotton and nitro-glycerine are made into a pulp with acetone, a little vaseline being also added. The pasty mixture is then forced through small holes in a steel plate, using hydraulic or screw pressure. The acetone evaporates, and the substance is obtained in the form of *cords* (whence the name), which are then cut into suitable lengths. These cords are made from about one to five millimetres in diameter, the smallest sizes being used for revolvers etc., the largest for heavy guns.

Besides the hexanitrate (guncotton) of which we have been speaking, cellulose forms lower nitrates which can be obtained by making suitable changes in the "nitrating" arrangements (*i.e.* the treatment with nitric and sulphuric acids). When these lower nitrates are dissolved in a mixture of alcohol and ether we have *collodion.* This substance is used in one of the processes for the manufacture of artificial silk. It is also used under such names as "new-skin" to form a protective covering over small wounds. The alcohol and ether evaporate, leaving the collodion as a firmly-adhering, transparent film.

By mixing these lower nitrates with camphor and placing the mixture in a hot press, *celluloid* is obtained,—a solid solution of camphor in the cellulose nitrates or of cellulose nitrates in camphor. It is used for making billiard balls, combs, umbrella handles, spectacle frames, and scores of other articles, but its great inflammability is sometimes a disadvantage.

Cellulose is the basic material not only for the substances we have been discussing, but also for the great paper and artificial silk industries which we shall consider in the next chapter. It is evidently an extremely important substance.

Questions

1. Calculate the percentage of carbon, hydrogen and oxygen in (i) starch, (ii) cane sugar.
2. A substance contains 40·0 per cent. of carbon, 6·7 of hydrogen and 53·3 of oxygen. When 9 gm. of it is dissolved in 100 gm. of water the solution freezes at —0·93°C. Find (i) the simplest formula, (ii) the molecular formula.
3. Calcium citrate, oxalate, tartrate, and tannate are practically insoluble in water. How is this fact turned to account in the preparation of sugar from beet-root?
4. Give some account of the manufacture of *either* starch *or* ordinary sugar.

5. There is only one substance having the formula CH_4, but there are two with the formula C_4H_{10}, seven with formula C_7H_{16}, and eighteen with the formula C_8H_{18}.
   Explain in a general way why the number of isomers increases with the number of atoms in the molecule.

6. How do you account for the facts that (i) the outside parts of an overbaked cake are black, (ii) milk turns sour much more quickly in warm weather than in cold, (iii) sugar leaves no ash when burnt?

CHAPTER XXIV

PAPER, RAYON, and RUBBER

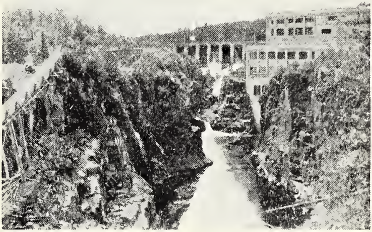
Modern methods of manufacturing paper require supplies of suitable wood, and (if possible) plenty of water power, —a combination which is suggested by the illustration on page 267. Canada is very well placed in both these respects, with the result that she is now easily the greatest producer of paper in the world. In 1930 her production of newsprint paper was nearly 2¾ million tons valued at over 150 million dollars. The next largest producer (the United States) has only about half this output, and, in fact, nearly half the paper used in U.S.A. is either of Canadian manufacture, or is made from wood or wood-pulp, which has been imported from Canada.

The rapid growth of the pulp and paper industries will be seen from the graphs on p. 268. Notice (Fig. 38) that although the production of pulp wood (chiefly spruce and balsam) has increased enormously, the amount exported has remained fairly constant, which means, of course, that Canada is using the increased supplies for her own manufactures.

The manufacture of paper really begins with the work of the lumberman. However, we shall take his operations for granted, and pass on to the conversion of the wood into pulp. This is effected either by a mechanical process or by a chemical one.

In the mechanical method the spruce or balsam, cut into four-foot lengths, is first run through revolving steel drums to remove the bark. It is afterwards washed, and conveyed to magazine grinders which feed the wood auto-

matically to revolving grindstones. Hydraulic cylinders press the wood against the stone on two sides, the wood having its axis parallel to the axis of the grindstone. The friction causes much heat to be generated, but this is controlled by running water over the stone, the water also serving to carry away the pulp in suspension. After screening to remove dirt and slivers (*i.e.*, splinters, etc. which have escaped thorough pulping) the pulp is ready for use in making newsprint.



By courtesy of Bathurst Power and Paper Co., Ltd.
Power plant for paper mill.

"Groundwood pulp" as the product of the mechanical process is called, is of inferior quality because it contains practically *all* the material of the wood. The best paper, however, consists only of cellulose, of which wood contains not more than 50 per cent. or so. The non-cellulose portion consists chiefly of a substance called *lignin,* having much the same composition as cellulose, but with different chemical properties. In the chemical process for manufacturing pulp, the lignin is removed, the chemical reagent used in Canada being chiefly calcium bisulphite, $Ca(HSO_3)_2$.

The barked and cleaned wood is fed end-on into the chipper machine, which cuts it across the grain into chips about five-eighths of an inch long. These are then "cooked"

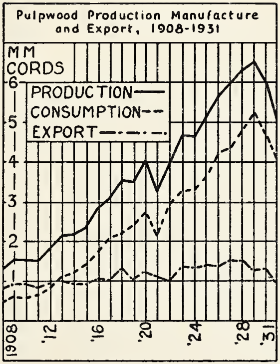


Fig. 38

N.B.—"MM" cords, *i.e.* vertical unit is 1,000,000 cords, a cord being 4 ft. × 4 ft. × 8 ft. of piled material, or about 90 cubic feet of solid wood.

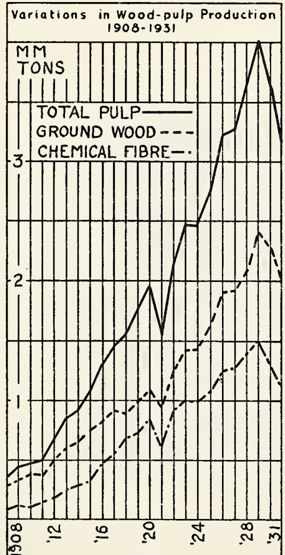


Fig. 39.

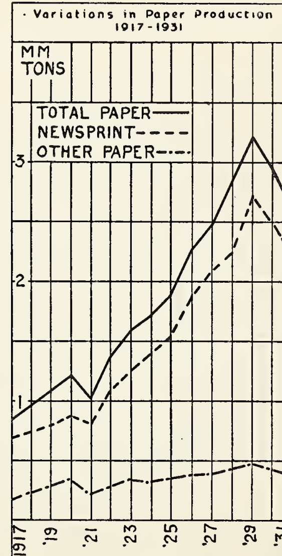


Fig. 40.

(*By courtesy of the Dominion Bureau of Statistics.*)

under pressure for about eleven hours, in digesters containing the bisulphite solution. These digesters are steel vessels lined with brick, and have a capacity of about fifteen tons each.

When the "cooking" is completed, the resulting pulp is blown out of the bottom end of the digesters, by steam pressure, through a large pipe into the blow-pits, where it is thoroughly washed to remove acid. After being screened it is then ready for use.

The pulp has now to be converted into paper. The best qualities would be made from "sulphite pulp" only, but newsprint paper would contain about 75 per cent. of groundwood pulp and 25 per cent. of sulphite pulp. In this case the two pulps are mixed with water in a regulating machine (a little alum and rosin soap, and sometimes coloring material, being added) and pumped through a pipe to the head-box or tank at the wet end of the paper machine. From the head-box the stock, including over 99 per cent. of water, is permitted to flow over a wire in a shallow stream. This wire is an endless belt 160 inches wide, of fine bronze-wire screen. It moves at the rate of about 900 feet per minute, carrying the stock forward towards the dry end of the machine. As it moves, the water runs through the wires, leaving the fibres of pulp on the wire in a thin sheet, which will form the sheet of paper. The wire also runs over suction boxes, in which a partial vacuum is maintained, to remove more of the water. After other processes intended to produce complete drying, the sheet passes through the calenders, which are a stack of large smooth steel rolls. These give the sheet a smooth surface and even thickness. The sheet is then wound on a shaft into a large roll, usually about 32 inches in diameter.

To save complicating the description, we have so far said nothing about the part played by the alum and the rosin soap. The latter is made by dissolving rosin in caustic soda. Rosin and aluminium hydroxide are precipitated in the pulp (the latter by hydrolysis). The

aluminium hydroxide serves to fill up the pores of the paper, while the rosin, melted by the hot rollers, gives it a surface. Without some such treatment the paper would cause ink to "run".

Notice that the quality of a good paper depends chiefly on the chemical inertness of cellulose (*cf.* p. 262). A really high class paper consists of nearly pure cellulose, and will remain in perfect condition for centuries. Paper containing much groundwood pulp, newsprint, for instance, soon becomes brown and rather brittle owing to the presence of lignin and some other substances, which treatment with bisulphite would have removed.

History.—We are so accustomed to the use of paper that we are apt to forget that it is really an invention, though it is certainly a very ancient one. The Chinese seem to have made it from fibrous material at least as far back as the second century B.C. From them the knowledge passed over to the Arabs, apparently as the result of a fight near Samarkand in 751 A.D., when the Arabs found that among their prisoners were two or three Chinese paper-makers.

From the Arabs the knowledge spread gradually over Europe, and paper was in use in England at least as early as the fourteenth century. Two centuries later blotting paper was evidently in use, for a book dated 1519 contains a passage the truth of which it is difficult to dispute,—"Blottyng papyr serveth to drye weete wryttynge lest there be made blottis or blurris."

Rayon.—Rayon, or artificial silk, as usually made, has one point in common with good paper,—it consists of pure cellulose. It is manufactured by four different processes, but we shall describe only one of them, the *viscose* process, which accounts for over 80 per cent. of the world output.

The raw material for the process is high grade bisulphite wood pulp (usually from spruce), about 40 per cent. of the world's requirements in this respect being supplied by Canada. After passing through a bleaching process, the

cellulose is treated for two hours with a 17 per cent. solution of caustic soda, which results in the formation of "alkali cellulose", said to have the formula $C_6H_{10}O_5 . H_2O . 2NaOH$. After squeezing out the surplus solution, the alkali cellulose is torn into crumbs which are allowed to mature for twenty four hours or more in a closed vessel.

Carbon disulphide is now added, when a viscous solution called viscose is obtained. After being allowed to "ripen" for a day or two, the viscose is ready for spinning. This is done by squirting the solution through fine holes into dilute sulphuric acid, the latter causing the fine jets of liquid, as they enter, to give an immediate precipitate of hydrated cellulose.

Improvements in the details of the process are constantly being made. A rather curious one is the production of hollow fibres instead of solid ones. One way of securing this is to add a small amount of sodium carbonate to the viscose. When the jet of viscose enters the acid, a minute bubble of carbon dioxide is first formed (by the interaction of acid and carbonate). The precipitated thread forms a tube round this bubble, and since each fresh portion of viscose as it enters the acid brings its quota of carbonate with it, the whole thread is tubular. It is found that these tubular threads rustle like real silk.

The viscose process was really discovered in instalments. As far back as 1844 John Mercer, a Lancashire calico printer, found that cotton cloth or yarn was shortened and strengthened when it was passed through a cold, strong solution of caustic soda. Forty years later it was discovered that if the material was stretched so that it could not shrink, the fibres acquired a silk-like lustre, and "mercerized cotton" became an article of manufacture.

A few years later C. F. Cross showed that on treating the mercerized cotton with carbon disulphide a yellow solution was obtained, and that on acidifying this solution a hydrated cellulose was precipitated. With these facts as a basis, Cross and Bevan in 1892 initiated the present viscose process.

Artificial silk differs entirely in composition from the natural article, and its tensile strength is much less, especially when wet (hence it would be very unsuitable for fishing lines). Still, it has a very good appearance, and this combined with its cheapness has caused it to be very widely used either alone, or as a mixture with wool or cotton.

Rubber.—Rubber is obtained from the milky juice (known as *latex*) present in some seventy different kinds of tropical and sub-tropical trees and shrubs. One of the

By courtesy of the Imperial Institute, London.
Tapping a rubber tree in Malaya.

best is known as the hevea tree and is native to Brazil. but in 1876 the botanist H. A. Wickham managed to smuggle some seeds out of the country, with the result that the tree now flourishes in Malaya, Java, and other parts of the East Indies. Until 1910 the world's rubber supplies were mainly derived from the forest trees of Brazil, the Belgian Congo, etc., but the great bulk of it is now obtained from the plantations of the East Indies.

The illustration shows a rubber tree being tapped. The latex is poured into vats and made to coagulate by the addition of acetic acid. The product is then placed in a machine which squeezes out most of the water and delivers a long continuous sheet known as crepe.

Pure rubber is stiff and hard when cold, but when warm becomes soft and sticky, so its uses would be very limited. These defects, however, are removed by treatment with sulphur, a process known as *vulcanizing*.

Rubber is a definite organic substance whose composition is expressed by the formula $C_{10}H_{16}$. It can be prepared synthetically, but the artificially prepared substance would be far too dear to compete with the natural product at present prices.

Although, of course, for climatic reasons, rubber cannot be produced in Canada, the manufacture of rubber goods,—notably automobile tires and rubber shoes—has developed into an important industry.

Questions

1. Calcium bisulphite may be made by adding calcium chloride to sodium sulphite solution (which precipitates calcium sulphite) and then passing sulphur dioxide through the precipitate, which then goes into solution. Write the equations.

2. On treating a solution of calcium bisulphite with excess of hydrochloric acid, 11·2 litres of sulphur dioxide (measured at N.T.P.) are produced. Calculate the weight of calcium bisulphite present. (1 gram-molecule of any gas at N.T.P. occupies 22·4 litres.)

3. The quality of paper made from linen rags is particularly good. Why should it be?

4. A substance contains 88·2 per cent. of carbon and 11·8 per cent. of hydrogen. Its molecular weight is 136. What is its formula?

5. "Cellulose, of which wood contains not more than 50 per cent. or so" (p. 267). How do you know, from observation of wood fires, that wood is certainly not pure cellulose?

CHAPTER XXV

ALCOHOLS, ACIDS, and ESTERS

Alcohols

In Chapter XXII we spoke of the *paraffin series,* hydrocarbons having the formulae CH_4, C_2H_6, C_3H_8 — or the general formula C_nH_{2n+2}. By indirect methods we can substitute an OH group for one hydrogen atom, and we thus obtain a new series $CH_3(OH)$, $C_2H_5(OH)$, $C_3H_7(OH)$ known as the *alcohols,* or strictly speaking, the *monohydric alcohols.* We must notice just one *tri*-hydric alcohol, namely glycerine $C_3H_5(OH)_3$, derived indirectly from propane C_3H_8 by the substitution of three OH groups for hydrogen atoms. There are alcohols derived from other series besides the paraffin series, but we shall not be concerned with them in this book. The alcohol of common speech is *ethyl* alcohol C_2H_5OH, but the lowest member of the series is *methyl alcohol,* CH_3OH. This was first prepared in 1661 by Robert Boyle who heated wood in a retort, and the commercial method of today is still the same in principle. *Wood charcoal* remains behind.

Methyl alcohol dissolves resins and shellac, and is therefore used in the preparation of varnishes. It is also used for adding to ordinary (*i.e.* ethyl) alcohol in order to make the latter undrinkable. The resulting "denatured alcohol" is in England called *methyl*ated spirit.

Methyl alcohol burns with a blue flame, being completely oxidized to carbon dioxide and water. You can easily write the equation. By a special arrangement, however.

it can be made to reach an intermediate stage of oxidation, when a gas known as formaldehyde, H . CHO is produced:

$$2CH_3(OH) + O_2 \rightarrow 2H.CHO + 2H_2O.$$

The reaction may be easily illustrated by the apparatus shown in Fig. 41. The flask contains a little methyl alcohol which has been gently warmed so as to produce a fair amount of vapour. The platinum spiral, attached to a glass rod which serves as a support, is removed, made red hot, and then quickly replaced. The reaction then takes place at the surface of the platinum, causing the latter to continue glowing, while the acrid smell of formaldehyde is quite perceptible.

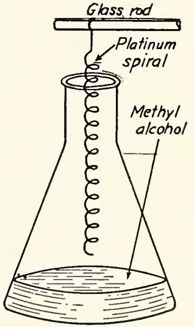


FIG. 41.—Production of formaldehyde.

A strong solution of formaldehyde is sold under the name of *formalin* and is much used as an antiseptic and disinfectant.

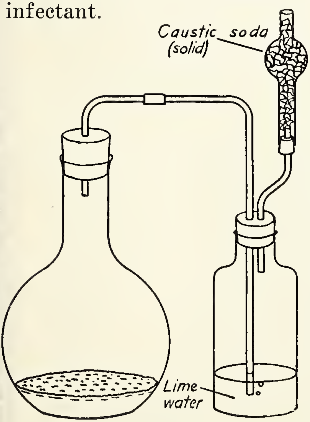


FIG. 42.—Production of alcohol.

Ethyl Alcohol, C_2H_5OH.—This is practically always produced by the fermentation of certain sugars. The process may be illustrated in the laboratory by dissolving 50 gm. of glucose in 500 c.c. of water, and putting the solution in a large flask (say 2 litres), afterwards adding about 10 gm. of yeast. The flask is then connected up as shown in Fig. 42 and is kept for at least 24 hours at a temperature of 25°C.—30°C.

There is much frothing, and the limewater turns milky, showing that carbon dioxide is being given off. By distilling off the first 20 c.c. or so, treating the latter with suitable dehydrating agents, and then distilling again, a small specimen of nearly pure alcohol may be obtained.

FIG. 43.—Yeast cells (highly magnified).

The reaction is expressed by the equation $C_6H_{12}O_6 \rightarrow 2C_2H_5OH + 2CO_2$, but nobody so far has really explained the part played by the yeast, though some progress has been made. We know that yeast is a low form of vegetable life, each individual plant being nearly spherical in form. The plants grow rapidly under such conditions as obtained in our experiment, but soon begin to produce buds which separate off, forming independent plants. It was long thought that the breaking down of the sugar into alcohol and carbon dioxide was necessarily connected with the life and growth of the plant. We know now that this is not the case, for Buchner has been able by pressure to abstract from the yeast a substance which he has called *zymase*, and which though a "dead" substance is able to ferment a solution of sugar. Up to the present, however, little is known of the composition of zymase, and nothing whatever of its mode of action.

Zymase cannot ferment cane sugar, but yeast is always accompanied by another ferment called *invertase*. The invertase first breaks down the cane sugar into the two simpler sugars dextrose and levulose (*cf.* p. 259)

$$C_{12}H_{22}O_{11} + H_2O \rightarrow C_6H_{12}O_6 + C_6H_{12}O_6$$

and the zymase is then able to bring about the fermentation. Because it acts by addition of the elements of water, invertase is known as a *hydrolytic ferment*. Hydrolytic ferments are often called *enzymes*.

When making alcohol on an industrial scale the first step is to prepare *malt*, because malt contains an enzyme called diastase which can convert starch into a sugar,

maltose, isomeric with cane sugar (*cf.* p. 257 where starch was treated with extract of malt). Malt is produced by exposing barley to warmth and moisture, so that it shall begin sprouting, and then heating it to stop the process.

The malt is now heated with starch and water at 60°—65°C, the starch being derived from corn, potatoes, etc. It is rapidly converted into sugar (maltose), and the solution can now be fermented with yeast and distilled much as in our laboratory experiment.

It is not really necessary to *add* starch (because a quantity is already present in the barley) and in making beer, whisky, etc., starch would not be added; but, of course, the yield of maltose, and therefore of alcohol, is smaller.

Alcoholic liquors which have not been distilled (*e.g.* wine and beer) cannot contain more than about 18 per cent. of alcohol, because when this concentration is reached the ferment ceases to act. To obtain higher percentages the liquid must be distilled, the distillate being then known as a *spirit*. Brandy, for instance, was formerly *brandwine*, —wine that has been "burnt" or distilled.

The discovery of alcoholic beverages was no doubt an extremely ancient one. In warm countries men would drink grape juice, and if this were left standing for a few days it would undergo alcoholic fermentation, the zymase being present in the "bloom" of the grape skin. Primitive man, however, was saved from the evils of spirit drinking, for he did not understand the process of distillation.

Most civilized countries try to keep the consumption of alcohol within reasonable limits by putting a heavy tax upon it, thus making it costly. The difficulty is that ethyl alcohol is required in many industrial processes,—the extraction of oils and the preparation of ether and chloroform, to mention only one or two,—and if alcohol were very expensive, such processes could hardly be carried on. The difficulty is fairly well overcome by allowing alcohol to be sold free of duty provided it has been "denatured"

by the addition of wood spirit, kerosene, bone oil, etc., ingredients calculated to make it utterly unpalatable, without interfering with its legitimate industrial use.

Alcohol is a colourless, pleasant-smelling liquid boiling at 78°C. It burns with a nearly colourless flame forming water and carbon dioxide, and is much used in "spirit stoves", etc. On p. 240 we saw that with sulphuric acid it may give the gas ethylene, C_2H_4.

By passing a mixture of air and alcohol vapour over platinized asbestos, *acetic acid* may be produced, the alcohol undergoing oxidation at the surface of the platinum—

$$C_2H_5OH + O_2 \rightarrow \underset{\textit{Acetic acid}}{C_2H_4O_2} + H_2O.$$

Acids

Acetic acid, produced as we have just seen by the oxidation of alcohol, is the second member of a homologous series which begins with formic acid CH_2O_2 and continues with $C_2H_4O_2$, $C_3H_6O_2$, $C_4H_8O_2$, and so on, the general formula being $C_nH_{2n}O_2$. We had better write this, however, as $H \,.\, C_nH_{2n-1}O_2$ to indicate that one of the hydrogen atoms behaves differently from all the rest. The difference is that only this one atom can be replaced by a metal, the acids of this series all being monobasic. The series is known as the *fatty acid* series because the higher members can be obtained from certain fats. Stearic acid, for instance, $H \,.\, C_{18}H_{35}O_2$, can easily be prepared from mutton fat.

All except the first two acids of the series exist in isomeric forms, which become very numerous with higher members of the series. Further, there are many other series of organic acids besides the one we are discussing, so the total must be enormous. We shall touch upon only one or two common ones.

Formic Acid, $H \,.\, CHO_2$, (Lat. *formica* = an ant) was so called because in the seventeenth century it was actually obtained by distilling ants! It is present in nettles and in the sting of bees, etc. It is very corrosive and soon raises blisters.

In the laboratory it is sometimes used in the preparation of carbon monoxide, for on heating with sulphuric acid it loses the elements of water. Hence we have $H . CHO_2 \rightarrow H_2O + CO$.

Acetic Acid, $H . C_2H_3O_2$.—A dilute solution of this acid, vinegar, has been known from the most ancient times. Wine and other alcoholic residues are apt to turn sour on exposure to the air, the chemical change being the oxidation of alcohol to acetic acid—

$$C_2H_5OH + O_2 \rightarrow H . C_2H_3O_2 + H_2O.$$

In making vinegar, the conditions are so arranged that this chemical change shall take place as rapidly as possible. It is found that (i) a particular ferment, *mycoderma aceti,* must be present, (ii) there must be free access of air, and (iii) a moderate temperature (about 37°C.) must be maintained. The process is a very interesting one, but we have not space to describe it here.

The acetic acid of commerce is not prepared from vinegar, but from the aqueous liquid obtained by the dry distillation of wood,—the same liquid from which methyl alcohol is obtained. In a more modern process the starting point is acetylene, C_2H_2, prepared from calcium carbide (p. 242). This is oxidized to acetaldehyde, C_2H_4O, and then to acetic acid. The plant of Shawinigan Chemicals Ltd. at Shawinigan Falls, Quebec, is capable of producing 50,000 tons of acetic acid per year by this process.

Tartaric Acid, $H_2 . C_4H_4O_6$.—This acid is dibasic, as we have indicated by placing H_2 apart from the rest of the formula. Calcium tartrate, for instance, would be $Ca . C_4H_4O_6$.

The potassium-hydrogen salt, $KH . C_4H_4O_6$, occurs in grape-juice. Though slightly soluble in water, it is practically insoluble in alcohol, so when the juice ferments the salt is precipitated, the crude deposit being known as "*argol*". After purification it comes into the market as *cream of tartar,* and it is from the latter substance that tartaric acid is prepared. It is much used in making

effervescing drinks, "health salts" and the like, which often consist of a mixture of this acid with sodium bicarbonate. On adding water we have—

$$H_2 . C_4H_4O_6 + 2NaHCO_3 \rightarrow Na_2C_4H_4O_6 + 2H_2O + 2CO_2.$$

Of the many other organic acids which are present in nature, either free or in combination (as salts), we shall mention only two. *Citric acid,* $H_3C_6H_5O_7 . H_2O$, is found in the juice of lemons, oranges, limes, etc., and *malic acid,* $H_2 . C_4H_4O_5$, is found in apples, gooseberries, and some other fruits. The formulae are given not to be learnt, but to make it clear that the acids represented do not belong to the "fatty acids"; neither, of course, does tartaric acid.

Esters

It is instructive to notice that in its behaviour with sulphuric acid, ethyl alcohol somewhat resembles sodium hydroxide.

Compare $C_2H_5OH + H_2SO_4 \rightarrow C_2H_5HSO_4 + H_2O$
with $NaOH + H_2SO_4 \rightarrow NaHSO_4 + H_2O.$

Then, corresponding to Na_2SO_4, we have a substance of formula $(C_2H_5)_2SO_4$, while C_2H_5Cl may be compared with NaCl.

The fact is that in some important respects alcohol does show basic properties, the group C_2H_5 (known as *ethyl*) behaving like a metal. Alcohol does *not,* however, turn litmus blue, and it does not readily neutralize acids when it mixes with them. Probably these differences are explained by the fact that unlike sodium hydroxide, it is not ionized in solution.

Before considering how ethyl alcohol *can* be made to react with acids, let us notice that the hydrocarbon group in other alcohols, *e.g.*, CH_3 (in CH_3OH), C_3H_7 (in C_3H_7OH), and so on, can also replace the hydrogen of an acid. The compounds obtained are not usually called salts, but *esters.* CH_3Br (methyl bromide) would be the ester

of an inorganic acid, while $C_3H_7 \,.\, C_2H_3O_2$ (propyl acetate) would be the ester of an organic acid.

Ethyl acetate is a very typical ester, so we shall give it a little consideration.

It is *prepared* by distilling a mixture of ethyl alcohol and acetic acid, to which sulphuric acid has been added—

$$C_2H_5OH + H \,.\, C_2H_3O_2 \rightarrow \underset{\textit{Ethyl acetate}}{C_2H_5 \,.\, C_2H_3O_2} + H_2O.$$

The action would be highly reversible were it not for the presence of the sulphuric acid which, owing to its great affinity for water, "binds" that liquid, so to speak. In making esters, sulphuric acid is used very often indeed for this particular purpose.

Ethyl acetate is a colourless mobile liquid boiling at 77°C. It has a pleasant, fruity odour which is very characteristic of an ester. In fact, the fragrance of flowers and fruits is often due to the presence of this class of compound.

Ester formation is obviously parallel to salt formation. Now by the action of water the process of salt formation may often be partly or completely reversed, and we call this reversal *hydrolysis* (p. 49). When a *large* quantity of water acts on bismuth chloride for instance, we have

$$BiCl_3 + 3H_2O \rightarrow Bi(OH)_3 + 3HCl.$$

Similarly, ethyl acetate (and other esters) may be hydrolysed—

$$C_2H_5 \,.\, C_2H_3O_2 + H_2O \rightarrow C_2H_5OH + H \,.\, C_2H_3O_2.$$

The hydrolysis is greatly accelerated by the presence of caustic potash, which combines with the liberated acid, so preventing a "right to left" action.

On p. 274 we referred to the trihydric alcohol, glycerine, $C_3H_5(OH)_3$, and an important ester is known of which the group C_3H_5 forms the "basic" part and stearic acid $H \,.\, C_{18}H_{35}O_2$ (p. 278) forms the "acid" portion. As C_3H_5 is trivalent (a point which is at once obvious from

the formula of glycerine) while $C_{18}H_{35}O_2$ is univalent, it follows that glyceryl stearate will be $C_3H_5(C_{18}H_{35}O_2)_3$. It is often given the shorter name *tristearin*. Similarly, glyceryl palmitate (*tripalmitin*) is $C_3H_5(C_{16}H_{31}O_2)_3$. We must also notice glyceryl oleate or *triolein*, $C_3H_5(C_{18}H_{33}O_2)_3$, though the acid in this case belongs to a different series.

At ordinary temperatures, tristearin and tripalmitin are comparatively hard fats, while triolein is an oil. Most common fats and oils contain one or more of these three substances, and are usually hard or soft according as they contain little or much triolein. Thus, beef suet, mutton fat, and tallow contain a high proportion of tristearin, while lard contains more triolein, and in olive oil the triolein greatly predominates.

When these fats and oils are hydrolysed with a solution of caustic soda, the alcohol (glycerine) and (sodium salt of the) acid are produced. Thus, with tristearin we should have—

$$\underset{\textit{Glyceryl stearate}}{C_3H_5(C_{18}H_{35}O_2)_3} + 3NaOH \rightarrow \underset{\textit{Glycerine}}{C_3H_5(OH)_3} + \underset{\textit{Sodium stearate}}{3NaC_{18}H_{35}O_2}.$$

This reaction and the corresponding ones with tripalmitin and triolein are the essential changes that take place in soap manufacture, ordinary soap being a mixture of sodium stearate, sodium palmitate, and sodium oleate. In broad outline, the manufacturing process is somewhat as follows. The fat is introduced into a large "soap pan" or "copper", which may have a capacity of as much as 30 tons. Inside this is a perforated coiled pipe, through which steam can be blown to heat the contents. Steam is passed until the fat is thoroughly melted, and then "lye" (a solution of caustic soda) is added in stages. The injected steam not only heats the mixture, but causes it to be thoroughly stirred. The addition of lye and the heating are continued until the operator finds (by the rather curious method of *tasting*) that the alkali is present in excess.

After boiling for a few minutes longer, a measured quantity of strong brine is added to the charge. This causes the soap to separate out on the surface, soap being insoluble in a solution of salt. The process is known as "salting out".

The spent lye is now run off from below, and after certain minor operations into which we cannot enter here, the soap is transferred to large frames, so that it may set hard. These frames consist of iron plates clamped together in such a way that when setting is complete, the sides can be removed. The large rectangular block of soap is then cut first into slabs and then into bars.

It has already been explained that glycerine is produced in the course of soap manufacture. It was formerly allowed to run to waste, but is now recovered as a valuable by-product.

Questions

1. Ethyl acetate is found on analysis to contain 54·5 per cent. of carbon, 9·1 of hydrogen, and 36·4 of oxygen. When 1 gm. of the substance was dissolved in 30 gm. of water, the latter was found to freeze at $-0{\cdot}705°$ instead of at 0°C. Find (i) the simplest, and (ii) the molecular formula of the substance.

2. You are asked to make an effervescing mixture of tartaric acid and sodium bicarbonate, and you have exactly 4 oz. of the former. How much sodium bicarbonate would you mix with it so that the two substances should be present in equational proportions?

3. What volume of carbon dioxide, measured at 27°C. and 74 cm. pressure, would be given off during the fermentation of 20 gm. of pure glucose, assuming the process to take place according to the equation on p. 276, line 7? (See note in italics, p. 20.)

4. Show that the number of alcohols, organic acids, and esters is likely to be very great indeed.

5. Explain the difficulty which confronts a government anxious to develop its manufactures, but also anxious to discourage the drinking of alcoholic liquors.

6. Explain the terms *enzyme, spirits, fatty acid, monohydric alcohol.*

7. One method of making an ester is to mix the appropriate acid and alcohol, and (while maintaining a suitable temperature) to pass dry hydrogen chloride through the mixture. What part is played by the hydrogen chloride?

8. One test for potassium ion is to add a strong solution of tartaric acid to a strong solution of the potassium salt, when a crystalline precipitate is produced. Of what do you think the precipitate may consist? Attempt an equation, supposing the potassium salt to be the chloride.

CHAPTER XXVI

FOODS AND VITAMINS

We take food for two chief purposes. One is to produce heat and kinetic energy,—the heat with which our bodies are always warm, and the energy which we use when we walk or run or work. In this respect the effect of food on our bodies is similar to that of gasoline on an automobile. It makes the engine warm (though this result is not specially desired) and it enables the car to move.

The second purpose is to make good the wear and tear of our bodies and to enable growth to take place. The body is built up of very tiny units called *cells* which are constantly wearing out and which have to be replaced. This replacement comes from food, and here the gasoline and automobile obviously afford no parallel. There is no brand of gasoline which will prevent tires wearing out, and certainly none which will help a little car to grow into a big one.

Now the number of varieties of food is, of course, enormous, and if we had to discuss all these varieties neither a chapter nor a volume would be of much use. Fortunately, these many kinds of food can nearly all be dealt with under three heads, *carbohydrates, fats* and *proteins,* and we must now give some account of the part played by each of these groups.

Carbohydrates formed the subject of Chapter XXIII, where we saw that they included the various sugars, together with starch and cellulose. They serve to supply the body with heat and energy. It has been shown by experiment that a gram of sugar (for instance) gives out exactly the same amount of heat whether it is burned in

a calorimeter or in the body. The muscles of the body have been compared to a furnace in which the sugar is converted into carbon dioxide and water, just as it would be if we threw it into the fire. Of course the *temperature* at which oxidation takes place is much lower when it takes place in the muscles (just as rusting takes place at a much lower temperature than burning). Further, as already indicated, part of the heat may be represented by its equivalent of kinetic energy; and so a man who is doing heavy muscular work needs much more food than a clerk sitting in an office.

We ought to know just a little of the changes that these carbohydrates—sugars, starch, and cellulose—undergo when taken into the body. Sugars of formula $C_{12}H_{22}O_{11}$ —cane sugar and maltose, for instance—are changed by certain enzymes into simpler sugars of formula $C_6H_{12}O_6$. We have already had the equation on p. 259. Starch is partly turned into the sugar maltose by an enzyme called ptyalin, present in the saliva. If we "bolt" starchy food there is, of course, no time for this change to take place, and unchanged starch passes into the stomach. Even if food has been well chewed, the change into maltose would hardly ever be completed in the mouth, but the saliva continues to act on the starch for some time after the food has entered the stomach. In any case, nature provides that after starchy food has left the stomach and entered the small intestine, it shall there meet with certain ferments, of which one completes the change into maltose, and another breaks down the maltose into simpler sugars as already mentioned. When these simple sugars ($C_6H_{12}O_6$) have been produced, they dissolve in the blood, which distributes them to the muscles and other tissues of the body which need them. If there is a surplus, the body has means of converting it into an insoluble substance called *glycogen*, $(C_6H_{10}O_5)_n$, sometimes called animal starch, and this is stored mainly in the liver. If still further supplies are available, they are stored up in various parts of the body as *fat*. That is why a farmer who wishes to fatten his cattle supplies them with plenty of carbohydrates, and

why a doctor who has to treat a corpulent patient sometimes tells him to "keep off" potatoes.

The body cannot digest cellulose (bran, for instance, or the numerous cell walls present in vegetables). That does not mean that this substance is useless, for by its mere bulk and in other ways it has a beneficial action upon the intestines. You have probably noticed that a farmer mixes chaff, bran, etc., with his horse's food, although the animal cannot obtain any nourishment from them.

We come now to the question of fats. Chemically, as we saw in the last chapter, these are esters of certain fatty acids, especially the higher ones. Tristearin or glyceryl stearate, $C_3H_5(C_{18}H_{35}O_2)_3$, present in mutton fat and beef suet, will serve as an example.

Although the formula may seem rather alarming, we can see at a glance that the only elements present are carbon, hydrogen and oxygen, so we are not surprised to learn that fats also, like carbohydrates, serve as sources of heat and energy. In the long run they are "burnt" to carbon dioxide and water, the body making use of the heat so liberated. A gram of fat when burnt—whether in a calorimeter or in the body—gives off more than twice as much heat as an equal weight of carbohydrate. Probably that is why fat is so much relished in cold countries. It is said that an Eskimo child, given the choice between a lump of sugar and a lump of fat, will choose the fat. Certainly most of us tend to avoid fat during the summer and to eat more of it in the winter.

A moment's thought will show that carbohydrates and fats could not possibly supply all the material required by the body. Each organ of the body—brain, muscles, liver, etc.—is made up of what is known as *tissue,* the tissue, in turn, being composed of cells. Now tissue is constantly wearing out and has to be repaired or replaced. Hence, food must include all the elements present in the tissues, and these (besides carbon, hydrogen, and oxygen) include a considerable amount of nitrogen, present in compounds

known as proteins. Compounds of phosphorus, sulphur, and other elements are also very often present.

The necessary nitrogen, sulphur, and often phosphorus and iron are obtained from a group of foods known as *proteins,* which may be roughly defined as all foods (except certain nitrogenous fats) which contain combined nitrogen. Common proteins are white of egg, gluten (the sticky constituent of wheat flour), and casein present in milk and cheese. Lean meat is also rich in protein.

Proteins contain carbon and hydrogen which can be oxidized, and so they can,—and do,—serve as sources of heat and energy. Their special use, however, is to replace worn-out tissue, as already mentioned.

Besides carbohydrates, fats, and proteins, the body needs certain mineral salts. The gastric juice, for instance, contains about 0·2 per cent. of hydrochloric acid, the chlorine of which is derived from common salt; and iron salts are necessary for the formation of blood. Occasionally we take mineral salts as such, as when we add common salt to an egg or other food. More often, however, they are present in sufficient quantity in ordinary food. Fruits and vegetables, for instance, often contain chlorides and phosphates.

Finally, we must not forget the great importance of *water.* Within the body chemical actions in great variety are constantly taking place, most of them in solution,—and water provides the solvent. Water, too, (as a constituent of blood) conveys materials from one part of the body to another; and it performs a number of other useful functions.

Milk.—Having considered in a general way the essential constituents of food, we must pay rather special attention to a food which contains all of them,—milk. It contains also those important and rather mysterious substances *vitamins* which we shall have to consider presently.

We shall begin with a table giving the composition of two kinds of milk.

	Human milk	Cow's milk
Water	88	86·9
Solids	12	13·1
Protein	1·6[1]	4·8[2]
Fat	2·9	3·5
Carbohydrate	7·0	4·0

[1] Chiefly lactalbumin. [2] Chiefly calcium caseinogenate.

For babies, milk is a perfect food, though for adults the proportion of water is too high,—they would have to drink a very large amount of milk to obtain the necessary amounts of protein, fat, and carbohydrate.

It is important to notice that cow's milk contains a higher percentage of protein than does human milk. Further, this protein is not of the same kind, and tends to form large indigestible curds in the stomach. For this reason, if it is necessary to feed a very young baby with cow's milk, the latter is diluted with water. This reduces the percentage of protein and diminishes the tendency to form large curds. The dilution, however, also reduces the percentages of fat and carbohydrate (which were not too large before), so a little cream and milk sugar are added to make up the deficiency.

Vitamins

For at least fifty years there have been people who doubted whether animals could remain healthy on a diet which included nothing but carbohydrates, fats, proteins, mineral salts, and water. The first really serious research on the subject was, however, not undertaken until 1912, when Sir F. G. Hopkins made a careful study of the feeding of rats. In one of his experiments he fed six young rats on carbohydrates, fats, etc., which had been very carefully purified, while another six rats of similar age, weight, etc., were given the same diet but with the addition of 2 c.c. of milk per rat per day. The difference

in the rate of growth was astonishing, as indicated by the accompanying graph; and after about three weeks the rats which were receiving no milk declined and died.

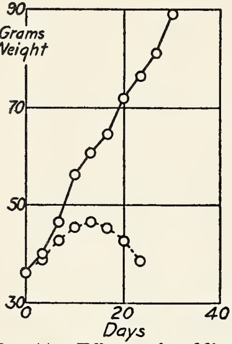


FIG. 44.—Effect of adding milk to the diet of young rats. (*By courtesy of Sir F. G. Hopkins and the "Journal of Physiology".*)

Now 2 c.c. of milk would contain about ⅓ gram of solid matter, and of this tiny amount nearly all is accounted for as fats, carbohydrates, etc., of which both groups of rats were receiving a sufficient supply in any case. We are driven to the conclusion that the 2 c.c. of milk contains in extremely minute quantity some other substance which is essential to growth and health. This mysterious substance is known as a *vitamin*. More recent work has shown that milk actually contains not one vitamin as was at first thought, but several quite distinct ones.

Up to the present, about half a dozen of these extraordinary substances have been recognized (not all of them in milk) and we must glance briefly at the more important ones.

Vitamin A is soluble in fats, and is present in milk, from which it passes into butter. It is also present in green foods and to a particularly large extent in cod-liver oil.

It is probable that it is somehow produced by green plants and sea-weed in the presence of sunlight, and that animals and fish obtain their supplies from this source.

This vitamin is concerned with growth, and with resistance to infection. Although it has not yet been isolated, a solution containing it has been prepared, and 0·005 to 0·01 mgm. of this solution will replace the 2 c.c. of milk mentioned above, *i.e.* added daily to a non-vitamin diet this amount will enable a young rat to grow and thrive.

Put in another way, 1 gm. per day of this extract would suffice for about 150,000 young rats!

It is interesting to note that 20 years ago the scientist was insisting that margarine was just as nourishing as butter, while the housewife protested that it was not. At that time nobody knew anything about vitamins,—but the housewife was right.

Some knowledge of *Vitamin B* really dates back to 1897 when Eijkman, the medical officer of a Java prison, was much worried by the prevalence of a disease called beri-beri among the men under his care. At the same time, curiously enough, many of the poultry in the prison grounds were dying from a complaint known as poly-neuritis, characterized by paralysis and certain convulsive movements. After much careful observation and experiment, Eijkman showed that the beri-beri and the poly-neuritis were due to the fact that both men and birds were being fed on polished rice,—rice from which the husk and germs had been removed. When "whole rice" was used instead, the disease did not appear.

Fifteen years later, when attention was being directed to vitamins, these results of Eijkman's were remembered, and it was shown that a definite vitamin (B) occurs in the germ and outer layers of wheat, rice, and other grains. It is very unlikely indeed that the function of vitamin B is *simply* to prevent the diseases mentioned above. Probably it serves in some way to maintain normal health, and indeed it is thought that it assists in regulating digestion. Vitamin B[1] is present not only in the germ of cereals, but also in yeast, eggs, nuts, and in tomatoes and some other fruits. To test whether a substance contains it, the experimenter observes whether it will cure a pigeon suffering from poly-neuritis. Yeast concentrates have been prepared which will effect this result with a dose of 0·1 mgm. per day. There is one famous case on record in which a cock,

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[1] It is now known that "B" is usually a mixture of two distinct vitamins, B_1 and B_2; but this account is not intended, of course, to be exhaustive.

paralyzed from poly-neuritis, was given a good dose of yeast at the beginning of a lecture on "Vitamin B", and just before the hour was up he struggled to his feet and crowed lustily, amid loud applause from the audience.

Vitamin C is rather widely distributed in the vegetable world, and is present in relatively large quantities in the juice of oranges, lemons, and tomatoes. For many years it had been recognized that scurvy, a disease which sometimes wiped out entire ships' crews in the old days of long voyages in sailing ships, rapidly cleared up when the sufferers were able to obtain a supply of fruit. It is now known that the disease was due to the absence of Vitamin C. No doubt this substance serves not only to prevent or cure scurvy, but to maintain health in less striking ways which are not at present understood.

Vitamin D is usually found associated with vitamin A in milk, cod-liver oil, etc., and in fact its existence as a separate vitamin was only recognized a few years ago. Its most striking property is its power of preventing and curing rickets, a disease in which the bones are soft, and become bent and mis-shapen as a result.

It is interesting to notice that vitamin D has actually been prepared in a pure crystalline condition, and at a medical exhibition held in London (England) in July, 1932, 120 grams of the substance were shown, packed in nitrogen in a sealed flask. Its anti-rickets potency is calculated as being equal to that of 10,000 gallons of cod-liver oil or 24,000,000 gallons of summer milk.

We have been able to touch only the merest fringe of a wide and constantly expanding subject. Obviously there will be further great developments. Complicated as they are, the vitamins are definite chemical compounds. The time will come when our chemists will be able to prepare all of them in pure form as they can already prepare vitamin D, and mankind will then be provided with new and powerful weapons for the cure and prevention of disease.

Questions

1. How far can food in its relation to the body be compared with gasoline in its relation to an automobile? Point out some ways in which the comparison breaks down.

2. It is said that crisp toast or biscuit is more digestible than stale bread, and stale bread more digestible than fresh. Why should this be the case?

3. Why does bread-and-butter figure so prominently in the daily food of most people?

4. Write equations representing the complete oxidation (to carbon dioxide and water) of (i) mutton fat, regarded as pure tristearin (p. 282), and (ii) cane sugar.

5. 100 gm. of cow's milk is diluted with 200 gm. of water to reduce the percentage of protein to that present in human milk (table, p. 289). What weight of cream and what weight of milk sugar should now be added so that the final composition should be as nearly as possible that of human milk? Assume that cream contains 50% of pure fat, and ignore the small change of volume produced by adding the cream and the sugar.

6. Suggest reasons why (i) vegetarians go in largely for dishes containing cheese; (ii) people who are "slimming" take their tea without sugar; (iii) a mouse prefers butter to margarine.

7. Lemon juice contains about 8% of citric acid, and up to the early years of the present century ships used frequently to carry supplies of citric acid to prevent scurvy, because it was inconvenient to carry lemons. In the light of present-day knowledge, what do you think of the practice?

Becquerel
Curie
Praut
Rutherford.
Sir Wm. Bragg

CHAPTER XXVII

RADIUM

It may seem strange at first sight that after discussing the chief metals in Chapters IX—XX and then passing on to other subjects, we should return in the present chapter to the study of another metal. The fact is that the discovery of radium has led to an astonishing advance in our knowledge of atomic structure, dealt with in the next chapter; and we cannot properly appreciate this advance unless we first know something about this curious element.

The story begins at least as early as 1896, when Henri Becquerel of the University of Paris was experimenting with salts of uranium. He happened to lay a crystal of one of these salts on a black paper in which was wrapped a photographic plate, and afterwards found that the crystal had photographed itself through the paper. Becquerel argued that the crystal must be giving off rays similar to the X-rays which had been discovered in the previous year by Röntgen. He next tried the effect of putting one of the crystals near a charged electroscope and found that the latter was rapidly discharged. A simple form of electroscope is shown in Fig. 45, where AB is a thin copper rod to which is attached a gold leaf CD. On giving the instrument a charge *via* the knob K, the mutual repulsion between the rod and the leaf causes the latter to stand out. When a crystal of the uranium salt is brought

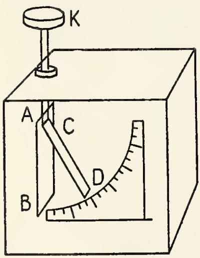


Fig. 45.—Electroscope.

near the knob, the leaf rapidly falls back. We shall see presently that the instrument can be used for the detection of radium, and a suitable type of electroscope will actually detect 10^{-12} gm. of this element. You may have seen a milligram weight (10^{-3} gm.), though these are not in very common use. It is very doubtful if one can visualize the thousandth part of this (10^{-6} gm.), but we should have to divide even this minute speck into 1,000 parts, and then one of these parts into 1,000 parts again, to get down to 10^{-12} gm.

However, let us return to the point at which Becquerel had observed some of the curious properties of uranium. These attracted the attention of Mme. Curie, and she interested herself in the subject. There might be other radio-active elements besides uranium, she thought, and with this in mind, she made a careful examination of a mineral known as pitchblende. From this she obtained a product which discharged the electroscope more rapidly than an equal weight of a pure uranium salt would do. Clearly something much more active than uranium was present. By further work she obtained something which seemed to be barium sulphate, but which was very radio-active. She decided that this product was most likely a mixture of barium sulphate with a radio-active sulphate. But if so, both were highly insoluble. How could she separate them?

She turned the sulphates into chlorides, dissolved these in water and crystallized out. Was the radio-active substance chiefly in the mother liquor or among the crystals? The charged electroscope would supply the answer,—it was chiefly among the crystals, for these had a much more powerful discharging effect. Apparently then, the radio-active chloride was less soluble than barium chloride, and so by re-crystallizing again and again she might effect a fairly complete separation. This she succeeded in doing, and after infinite labour found that from the original ton of pitchblende she had obtained about a third of a gram of a substance which was some two million times as radio-active as uranium. The new metal (of which she had so

far obtained only the chloride) she called radium. The metal itself was obtained some years later (in 1910) by electrolysis of a solution of the chloride, using a mercury cathode. With this the radium formed an amalgam which was distilled in a current of hydrogen, whereupon the mercury was volatized and the radium was left behind.

It is important to grasp the fact that radium is an *element* of the calcium-strontium-barium group (p. 143). Thus, it decomposes water with evolution of hydrogen, it has a definite atomic weight, and it forms a sulphate which is even less soluble than barium sulphate.

Yet radium has properties quite unlike those of any element we have so far discussed. It is constantly giving off rays, which by the action of a powerful magnetic field can be shown to be of three different kinds (Fig. 46).

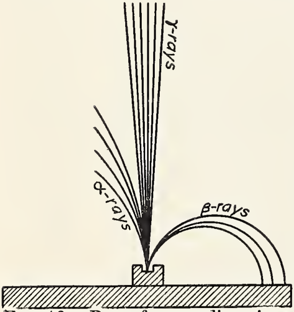


FIG. 46.—Rays from radium in a magnetic field.

One group, the alpha-rays, consists of positively-charged particles, while a second group known as the beta-rays carries a charge of opposite sign. The third group (gamma-rays) is not deflected at all by a magnetic field.

Further examination shows that the *α*-rays are really helium atoms each carrying two units of positive charge (what this unit is we shall see in the next chapter). Their velocity is roughly one-twentieth that of light, or say 20,000 times the muzzle velocity of a rifle bullet. As they strike the molecules of the surrounding medium their kinetic energy is partly converted into heat, and this accounts for the fact that radium is always slightly hotter than its surroundings. One gram of this peculiar element gives out 130 calories per hour, so that it would raise its own weight of water from room-temperature (say 15°C.) to boiling point in about 40 minutes.

The -particles are electrons, of which we shall have something to say in the next chapter, while -rays are found to be identical with X-rays, and are no doubt set up by the impact of the electrons on the matter lying in their path.

It has also been found that radium is constantly giving off some peculiar kind of gas. This can be swept away by means of a current of air, and passed into strongly cooled tubes in which it condenses. It turns out that this "emanation" is another element now called *radon,* of atomic weight 222! It seems then that the element radium, whose atomic weight is 226, when giving off another element, helium, of atomic weight 4, produces at the same time a third element, radon, of atomic weight 226 *minus* 4, or 222.

Radon itself is very unstable, splitting off helium and leaving a substance known as the *active deposit,* which is also unstable. Further changes take place, and the final product is a lead of atomic weight 206. The last six words evidently require some explanation, for the atomic weight of lead is given in the table at the end of the book as 207·2. That explanation will probably suggest itself after you have read the next chapter.

Clearly the outstanding point is that an element of high atomic weight can actually break up into elements of lower atomic weight. This is quite contrary to the Daltonian idea of the atom as a simple, unchangeable unit, and scientists were driven to probe into the question of atomic structure. That is why the discovery of radium marks the beginning of a new scientific era.

Questions

1. From the fact that radium compounds form crystals having the same shape as those of corresponding compounds of barium, it is concluded that radium has the same valency as barium, *i.e.* 2. Radium chloride contains 76·1 per cent. of the metal. What value does this give for the atomic weight?

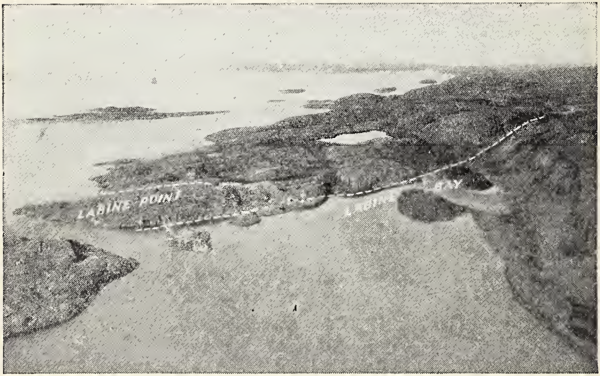
2. Honigschmid found that 100 parts by weight of radium bromide, $RaBr_2$, could be converted into 76·95 parts by weight of the chloride. Find the atomic weight of radium. ($Cl = 35{\cdot}46$. $Br = 79{\cdot}92$.)

3. You are prospecting near the Great Bear Lake for radium-bearing minerals. What test would you apply to the samples you collect? To what mistakes might your method lead?

4. Show that the solubility of radium sulphate is about what you would expect in view of the solubilities of the sulphates of calcium, strontium, and barium (*cf.* p. 143).

5. "The radio-active chloride was less soluble than barium chloride" (p. 295). Is this what Mme. Curie would expect? *N.B.*—The solubilities of strontium chloride, barium chloride, and calcium chloride at 0°C. are respectively 44·2, 30·9, and 59·5.

6. Say what you can of the respects in which radium (i) resembles, (ii) differs from, the more familiar elements.



Aerial view of LaBine Point, Great Bear Lake, looking north, showing the spot (marked x) at which pitchblende (radium ore) was discovered by Gilbert LaBine in May, 1930. The approximate course of the pitchblende veins is shown by the dotted lines. There are indications that further quantities occur in the pre-Cambrian shield, covering 12,000 square miles of Alberta. Some high authorities consider that the Canadian pitchblende deposits may well prove to be the richest in the world. The ore is being refined at Port Hope, Ontario. *Photograph by Royal Canadian Air Force Courtesy of Department of Mines, Ottawa.*

CHAPTER XXVIII

THE STRUCTURE OF THE ATOM

In the last chapter we saw that radium with an atomic weight of 226 is constantly giving off positively charged atoms of helium (atomic weight 4), at the same time evolving radon of atomic weight 222. We saw further that radon gives off helium, and that after a number of other changes the final product is lead of atomic weight 206. The difference between 226 and 206 is 20, suggesting that in five of the changes helium has been evolved, and this is in agreement with the results actually observed.

All this sets one speculating as to whether the radium atom (and presumably other atoms) are made up of helium atoms, and perhaps even of hydrogen,—each helium atom being regarded as a little packet of four hydrogen atoms. Is it possible by giving heavier atoms a really good *knock* to make them yield hydrogen atoms? A few years ago Rutherford decided to try. Alpha particles travelling at something like 10,000 miles a second should, he thought, have plenty of hitting force, so he used these as projectiles with which to bombard atoms of aluminium, nitrogen, and some other common elements. Among the products obtained he was able to detect positively charged hydrogen atoms! (The reason for "positively charged" will appear later.)

A suspicion that all atoms are built up of hydrogen is by no means new. In 1815 a Dr. Prout, noticing that atomic weights seemed to consist mostly of exact whole numbers ($H = 1$), put forward the suggestion that all atoms were aggregates of hydrogen atoms. "Prout's Hypothesis" aroused much interest, and to test its truth,

great attention was paid to the exact determination of atomic weights. The proportion of "whole number" results which turned up was certainly remarkable, but there were many exceptions. Chlorine in particular with an atomic weight of 35·457 was a case which could not be explained away, and the hypothesis ceased to be regarded seriously.

Very recent results, as we have just seen, appear to lend much support to Prout's idea. On the other hand, there are awkward cases such as that of chlorine. What are we to make of the contradiction?

To understand how the problem was attacked we must go back to some experiments carried out by various workers (in particular Sir William Crookes) about the year 1876. A tube arranged somewhat as in Fig. 47 was employed. It could be exhausted by means of an air pump, and a great difference of potential between A (anode) and C (cathode) could be obtained by connecting them with the positive and negative sides respectively of an electrical machine or of an induction coil. At very low pressures

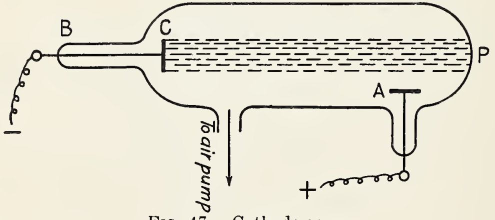


Fig. 47.—Cathode rays.

(about 0·01 mm.) a phosphorescent patch appeared at P opposite the cathode, and Crookes shewed that this was caused by a stream of negatively-charged particles travelling in straight lines from C. By using a perforated cathode, Goldstein proved that positively-charged particles were travelling from the cathode in the opposite direction, *i.e.,* in the direction CB, and it is these particles that for

the moment we wish to consider. They were carefully studied by Sir J. J. Thomson, and he showed that in their simplest form they were positively-charged *atoms* of the gas with which the tube had originally been filled (remember the tube was not *entirely* exhausted). The work was carried much further by Dr. F. W. Aston, and we shall see how his method worked out in the case of chlorine, though he examined many other elements besides.

His apparatus was so arranged that the positively-charged atoms of chlorine from the Crookes tube had to pass first through an electric field and then through a magnetic one at right angles to it, finally striking a photographic plate. Suppose P is the point at which a positively-charged particle, if it had undergone no deflection, would have struck the plate. The electric field alone would have produced such a deflection as to make it strike the plate at Q, while the magnetic field alone would have deflected it in a direction at right angles, and made it strike at R. Under the action of both fields it moves in the direction of the resultant force, and strikes the plate at S.

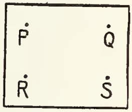


Fig. 48.

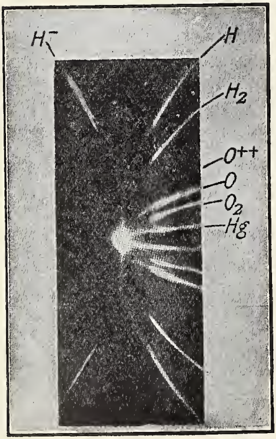
We shall suppose for the moment that the chlorine particles are all exactly similar except as regards velocity. A particle travelling at infinite speed would "get through" without any deviation at all, striking the plate at P. There are, of course, no particles of such speed, but the faster ones will strike nearer to P, the slower ones further away, and a mathematician can show very easily that their locus will be a parabola of which P is the vertex. He can also show that if some of the particles are of mass m_1, some of mass m_2, some of mass m_3, and so on, there will be a corresponding number of distinct parabolas.

In the case of chlorine, Aston obtained *two* parabolas, and by making certain measurements of these he found that m_1 was 35 and m_2 37, these being compared with the parabola given by oxygen, for which m would be 16.

So there are *two* chlorines, one of atomic weight 35 and another of 37. Ordinary chlorine is simply a mixture of the two, in such proportions as to give the value 35·457 for the atomic weight, and one of the chief difficulties connected with Prout's hypothesis disappears.

Many other elements besides chlorine consist of more than one form differing only in atomic weight (not in chemical properties—that is why it is impossible to separate them by ordinary means). Such forms are known as ***isotopes***. In many cases, though not in all, the isotopes have "whole number" atomic weights. One of the most remarkable exceptions is hydrogen itself, which on the "oxygen = 16" scale has an atomic weight not of 1, but of 1·008. This point will be considered later in the chapter.

In our study of atomic structure we have now met with considerable evidence that all atoms are aggregates of hydrogen atoms. It is certain, however, that this is not the whole truth. To begin with, these hydrogen units appear always to be positively-charged (*cf.* Rutherford's work on aluminium, nitrogen, etc., mentioned on p. 299). But how could a group of positively-charged hydrogen atoms, of themselves, make up an atom? A very elementary knowledge of electricity tells us that they would repel one another, and an atom so constructed could not hold together for a second. Further, *negatively*-charged particles are given off from radium, and so must have been present in the radium atom. Again, to go back once more to Crookes' experiment, his



From Aston's "Isotopes" by permission of Edward Arnold & Co.
Typical Positive Ray Parabola.

stream of negatively-charged particles (p. 300) — the "cathode rays" — have been found to be identical *no matter what gas is present in the nearly exhausted tube.* In all cases they have a weight equal to about 1/1850 of the weight of a hydrogen atom, and this is also the weight of the β-particles given off from radium.

Taking all the facts together, it seems clear that these negatively-charged particles, of almost negligible weight even compared with a hydrogen atom, are a constituent of all atoms. We can now see why an atom made up of positively charged hydrogen units does not fly apart. Some, at least, of these smaller particles, "electrons" as they are called, are engaged in holding them together. Such electrons (we shall see presently that not all of them are so occupied) are known as "cementing electrons".

Now an atom consisting of these "hydrogen" units held together by electrons would be a very compact structure, though, of course, extremely small. Yet Sir William Bragg found that when he bombarded such atoms with α-particles the latter usually went clean through. Making all allowances for the space between one atom and another, Bragg was able to show that his α-particles were actually going *through the atoms themselves,* though now and then one had evidently struck[1] something substantial, for it rebounded[2] like a billiard ball.

He came to the conclusion that the *substantial* part of the atom, the part containing the hydrogen units held together by the electrons, was really very small compared with the size of the complete atom. The facts would be covered by supposing that a heavy, positively charged centre, or nucleus, was surrounded at comparatively great distances by a number of electrons (not the cementing ones, of course), much as the sun is surrounded by the planets. Just as the diameter of the solar system is very great

[1] Or rather had come so close to it as to experience very violent repulsion (due to the proximity of like electric charges).

[2] The method by which the tracks of these α-particles were photographed is a most interesting one, but we have not space for it here.

compared with that of the sun, so the diameter of the atom is very great compared with that of the nucleus. Further, the sun contributes most of the *weight* of the solar system, and the nucleus contributes most of the weight of the atom.

Of the large amount of other work which has been carried out, bearing on the subject of atomic structure, we must make a brief reference to that conducted by H. J. G. Moseley. Moseley was only twenty-eight when his brilliant career was brought to an end by a Turkish bullet in the trenches of Gallipoli on August 10th, 1915, just a day or two before the arrival of orders for him to return to England to carry out further research. The loss to science is one that can hardly be measured.

To understand his work, we require some knowledge of spectra, a subject which is dealt with in works on Physics. Here we will only recall that elements (and their compounds) when strongly heated can be made to give certain lines in the visible spectrum, and that from the position of these lines the wave length of the light which produced them can be calculated.

Moseley succeeded in obtaining *X-ray* spectra of various elements. Such spectra, of course, cannot be seen—we are not dealing with light,—but the position of the lines in them may be found by photographic and other methods. He found that all the elements he tried gave similar but not coincident spectra, *i.e.,* the lines in one spectrum would be so much to the right or left of the corresponding lines in another. Selecting a particular line (known as the α -line) in each spectrum he examined, Moseley was able to calculate the wave length of the X-rays which produced it, and from this he easily obtained the frequency v (*i.e.,* the number of vibrations per second). After making a number of experiments he discovered that $v = k(N-1)^2$, where k is a constant ($= 82{,}258$) and N is the ***atomic number,*** *i.e.,* the number indicating the order in which the element stands in the Periodic Table (*e.g.,* the atomic number of

hydrogen, helium, and lithium would be 1, 2, and 3 respectively).

It is interesting to notice that by Moseley's method the atomic number of potassium works out at 18 (*cf.* table pp.68-9). This brings it to its correct place in the Periodic Table, though if arranged in order of atomic weight potassium comes out of place (*cf.* p. 73). The fact is that argon (39·9) contains two isotopes of atomic weights 40 and 36, and potassium (39·1) also two, of atomic weights 39 and 41. If we compare the lighter argon (36) with the lighter potassium (39), and the heavier argon (40) with the heavier potassium (41), we see that argon would precede potassium in each case, and there would be no irregularity. It so happens, however, that ordinary argon consists chiefly of the heavy variety (40) and the ordinary potassium mostly of the lighter kind (39), so that ordinary argon proves to have a higher atomic weight than potassium.

Iodine and tellurium, cobalt and nickel also take their right places in the table if arranged in accordance with their atomic numbers, though they are out of place if arranged in order of atomic weight.

It is clear, then, that while the properties of an element are *usually* related to its atomic weight, they are *always* related to its atomic number. Atomic number is a more fundamental property than atomic weight.

Keeping in mind the relationship $v = k(N-1)^2$, it is obvious that from the X-ray spectrum for any element (which gives v) we can at once calculate N. As Soddy says, we are now able "to call the roll of the chemical elements and to determine how many there are and how many remain to be discovered". Between hydrogen and uranium there are 92 possible elements, of which in 1913 six remained to be found. All have now been identified except two, these having atomic numbers 85 and 87 respectively.

With his results as a basis, Moseley was able to reach certain conclusions which are easy enough to understand, though the reasoning which led to them is outside the scope of this book. He concluded that taking the charge on the hydrogen nucleus as unity, the net positive charge on the nucleus of any atom is equal to the atomic number. But the atom as a whole is electrically neutral. Therefore, outside the nucleus there must be a negative charge (due to the presence of electrons) also equal to the atomic number. An illustration will make the point clear. Lithium has an atomic weight of 7, and an atomic number of 3. Its atomic weight being 7, the nucleus must contain seven positively-charged hydrogen atoms ("protons" as they are often called). But the net charge is to be 3 (= atomic number). Therefore, there are four nuclear electrons, and the net nuclear positive charge of 3 is neutralized by the negative charge of the three "planetary" electrons.

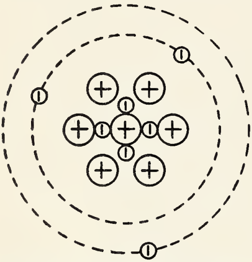


FIG. 49.—The lithium atom (diagrammatic only).

It will be seen that this conception of the structure of the atom is quite in keeping with that deduced from Bragg's experiments (p. 303) but we are now able to express the matter quantitatively. The atom is still regarded as a tiny "solar system", and indeed the electrons are believed to revolve round the nucleus, though possibly in "spherical shell" orbits rather than in planes.

Let us now consider how our new views of the atom help us to explain one or two facts that would otherwise be very puzzling. We shall first deal with the regular change in valency observed as we pass from Group O to Group VII of the Periodic Table (pp. 68-9). Taking in order the first eight elements that follow hydrogen (*i.e.* helium to fluorine), we may represent the planetary electrons thus:—

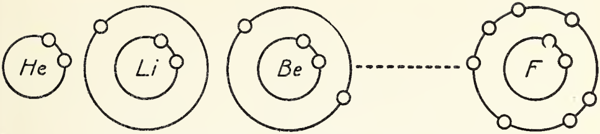


FIG. 50.—Arrangement of planetary electrons.

Notice that in the diagrams given above we have shown an inner orbit of two electrons, and placed the additional electrons in an outer orbit. There is good reason to believe that an inner ring of two electrons represents a very stable arrangement,—one not easily disturbed,—and that *eight* electrons in an outer orbit are also very stable.

After the 2—8 system is complete, a third orbit begins to be built up. Thus, we have Ne 2.8.0, Na 2.8.1, Mg 2.8.2, Al 2.8.3, Si 2.8.4, P 2.8.5, S 2.8.6, and Cl 2.8.7 (*i.e.* 2 electrons in the inner orbit, 8 in the second, and 7 in the third).

Now suppose an atom of sodium meets one of chlorine. The sodium atom (2.8.1) says (we may imagine), "I should feel much steadier without this outer electron." The chlorine atom (2.8.7) replies, "And *I* should be much steadier with an extra one. It would just make up my outer orbit to 8." So the sodium atom loses an electron to the chlorine, and with the formation of sodium chloride both achieve stability. (Incidentally it is worth noticing that as the sodium atom, formerly neutral, has lost a *negative* electron, it will now be electro-*positive*. Similarly the chlorine will be electro-negative. These electrical characters become obvious, of course, when a solution of sodium chloride is electrolysed.)

You can easily work out other cases for yourself, *e.g.* if magnesium and chlorine meet, there will be stability for both if *one* atom of magnesium loses *two* electrons, and *two* atoms of chlorine each gain *one*. Thus 1 atom of magnesium will combine with 2 of chlorine, forming $MgCl_2$, *i.e.* magnesium will behave as a divalent element. We see now why the valency steadily advances as we pass along the horizontal

lines of the Periodic Table. We can also see why helium (2.0) and neon (2.8), already stable, have no "inducement", so to speak, to combine with other elements.

Notice that phosphorus (2.8.5) can achieve stability in two ways, either by losing 5 electrons (becoming 2.8) or by gaining 3 (becoming 2.8.8). The first change would be represented by the formation of phosphorus pentoxide, P_2O_5, the second by the formation of phosphine, PH_3. In the same way we can account for the existence of such pairs of compounds as N_2O_5, NH_3; CO_2, CH_4; SH_2, SO_3; ClNa, Cl_2O_7. The fact that under certain conditions the sum of the two valencies comes to 8 is known as Abegg's Law, but we can do no more than give it a passing mention.

Matter and Energy.—We must now take up a curious point to which reference has already been made. The atomic weight of helium is 4 (on the "oxygen=16" scale). Why is the atomic weight of hydrogen 1·008 instead of 1?

Represented diagramatically we may put for the respective atoms

and

Helium Hydrogen

FIG. 51. (diagrammatic only.)

Hydrogen contains one proton and one electron, helium four protons and four electrons (two nuclear and two planetary). Surely the helium atom should weigh *exactly* four times as much as the hydrogen atom?

But to turn hydrogen into helium it would not be sufficient to put four atoms (or two molecules of H_2) together. We should have to *re-arrange* the protons and electrons,

It has been shown that if this could be done, energy would be liberated, and that this gain of energy would be accompanied by a loss of matter, 4·032 units being reduced to 4. The energy change would be enormous. It has been calculated that the conversion of one gram of hydrogen into helium would liberate energy equivalent to 200,000 kilowatt-hours. On this basis three ounces of hydrogen in the process of its conversion could be made to drive a 50,000 horse-power liner from Montreal to Liverpool and back again, leaving an ample reserve for emergencies.

But we have not the least idea of how to convert hydrogen into helium!

Only a few years ago men smiled pityingly as they read of the long-continued effort of the alchemists to turn base metals into gold. Yet in a way the alchemists were right. Gold and lead and iron are all made up of protons and electrons, and so the quest was not necessarily hopeless, however great might be the practical difficulties. Of far more practical use, however, would be the discovery of how to turn matter into energy. Countries would then cease to make anxious investigations into their resources of coal and oil and of water-power; but whether mankind has advanced sufficiently to make a wise use of such a discovery is more than doubtful.

Questions

1. What are *isotopes?* From the list at the end of the book pick out four elements which probably form no isotopes. What guides you in making your selection?
2. What evidence is there that atoms contain (i) protons, (ii) electrons?
3. In what respects is the structure of an atom well illustrated by the solar system? Can you see any defects in the illustration?
4. In the periodic table there is an irregularity associated with argon and potassium. What is it and how do you account for it?

5. There appear to be no elements beyond uranium (atomic weight 238 and atomic number 92). Why should there be a limit?

6. Fig. 51 on p. 308 shows the protons and electrons in an atom of lithium. Give a similar representation of an atom of carbon.

7. Hydrogen combines readily with fluorine, and when the hydrofluoric acid so produced ionizes, the hydrogen ions have a positive and the fluorine ions a negative charge. Account for these facts in terms of the electronic theory of atomic structure.

CONCLUSION

WHAT OF THE FUTURE?

In the foregoing pages an attempt has been made to give a general idea of the way in which chemistry has developed, both on the side of theory and in its practical applications to the daily life of man. A very natural question is to ask ourselves "What next?" and in these closing paragraphs we shall consider some developments that may sooner or later be expected to take place.

First of all, however, we shall glance backwards for a moment, and we notice that man has passed through a Stone Age and a Bronze Age, and may now be said to have reached the Steel Age. Will the metal that he chiefly uses continue to be iron?

Iron modified into the various steels has some very wonderful properties, as we saw in Chapter XVI. Its defect, of course, is its tendency to rust. Aluminium is, for practical purposes, free from this drawback, and has the further great advantage of having only about one-third the density of steel; but it has nothing like the same tensile strength.

If a cheap rustless steel can be made, suitable for large constructional work, this metal will probably continue to hold its own. On the other hand, aluminium alloys possessing great toughness and tensile strength are already being prepared, and still better ones will be produced. Further, the future will almost certainly see aluminium manufactured very cheaply from clay. There is no doubt that both steel and aluminium will continue to hold their own for certain special purposes, but which will emerge as *the* metal of the age remains an interesting question.

Turning now to the subject of food supplies, we have seen that the chemist has already done a great deal by showing how an abundant supply of nitrogenous fertilizers may be obtained, while for many years the world's chemical works have produced ample quantities of the necessary phosphates. The next step consists of discovering how to make cheap potash fertilizers from feldspar. Canada, for instance, has almost unlimited supplies of the latter substance, and yet she has to import something like 20,000 tons of potash fertilizers per year.

For the solution of the potash problem we shall probably not have very long to wait. A much more difficult problem is concerned with the texture of the soil, and can best be made clear by considering the results of an experiment made at Rothamsted experimental farm in England. Of two similar plots *A* and *B* producing barley, *A* received farmyard manure for 21 years (1852 to 1872), while *B* received none. For the last 60 years neither plot has received any manure, yet *A* still produces about 50 per cent. more barley than B.

It seems likely that the long-continued beneficial effect of the farmyard manure is due to the colloidal material which it imparts to the soil. At present the chemistry of colloids is, comparatively speaking, still in its infancy, and we shall probably have to wait a long time before the chemist can show us how to prepare artificially substances which will have just as good an effect.

Closely connected with the subject of food supplies is that of vitamins, already discussed in Chapter XXVI. Here there will certainly be great developments—in fact they are taking place now. We may expect new vitamins to be discovered, and in every case the chemist will endeavour (i) to isolate the substance—there may be only a few milligrams of it in say a ton of food material, (ii) to find exactly how its molecule is built up, and (iii) to synthesize it from common substances of simple composition, or even from its elements.

This will involve many years of work by chemists of the first rank, but in the end it will be possible to manufacture the necessary quantities of any given vitamin. By that time the doctors will probably have traced a considerable number of diseases to shortage of particular vitamins, —just as they have done already in the case of rickets, scurvy, etc.,—and these "deficiency diseases" will then cease to trouble us.

In its relation to medicine, however, chemistry will find a much wider field of service than that just indicated. The fact is that the chemical processes taking place within the body are very numerous and often extremely complicated. At present our knowledge is as nothing in comparison with our ignorance, but as our knowledge increases, so will our control over disease. Just one example must suffice. At the base of the neck, in front, there is the thyroid gland which manufactures a complex substance known as thyroxine. If for any reason the gland fails to manufacture the proper amount of thyroxine, a number of very serious results follow. One of them is a disease known as cretinism, in which the patient is practically an idiot. He grows very little, seldom reaching a height of more than 4 feet, and his skin feels thick like dough. There are other terrible features of this disease, but doctors with the help of chemists have proved that all the trouble is due to the fact that the thyroid gland is not manufacturing thyroxine, or not manufacturing enough. Thyroxine can be obtained from the thyroid glands of sheep and it can now also be prepared in the laboratory. Most wonderful results have followed when "cretins" have been dosed with it. They begin to grow rapidly, develop a healthy skin and cease to be idiots. If such results can be obtained with the slight knowledge we have at present of the chemical processes taking place within the body, we may confidently expect that when that knowledge becomes really considerable it will be possible to prevent or cure diseases to an enormously greater extent than is the case at present.

Let us consider next how far the chemist will be able to help us in connection with our supplies of power, derived chiefly at present from coal and oil, and in some countries (*e.g.* Canada) from water. Here it is important to realize that the best type of internal combustion engine, *i.e.,* one in which the fuel is burnt *inside* the cylinder, as in an automobile, is just about twice as efficient as the best type of coal-burning engine, in which the fuel has to be burnt outside. The obvious course seems to be to turn coal into gasoline if it can be done,—and it can. As we saw in Chapter XXII, gasoline is a mixture of hydrocarbons having formulae such as C_5H_{12}, C_6H_{14}, etc. Coal contains a much smaller proportion of hydrogen. By treating coal with hydrogen under suitable conditions of temperature and pressure excellent gasoline can be obtained, and the only reason the process is not worked is that the manufactured product could not compete with natural gasoline at its present low price. However, it seems certain that the world's supplies of natural oil will give out long before its coal supplies, and manufactured gasoline will then find a ready market. It is worth noting that soft coal and bitumen are more readily hydrogenized than hard coal, and this suggests a great future for the immense bituminous deposits of Alberta.[1]

The developments so far indicated—and others might have been added—may be regarded as reasonably certain to take place sooner or later.

The possibilities at which we hinted at the close of the last chapter are, of course, of a far more problematical character. As all atoms are composed only of protons and electrons there is no *absolute* reason why the chemist should not manufacture any substance he pleases out of any other. All the protons and electrons necessary for manufacturing

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[1] Gasoline can be obtained from bitumen by cracking and distilling p. 250) leaving a residue still richer in carbon. In a perfect hydrogenization process, however, the whole of the carbon would be used up, and, of course, the yield of gasoline would be very much greater than in the distillation process.

platinum, for instance, or gold or silk, are present in a log of wood, or in water or common earth. The type of change suggested, however, is sharply marked off from the ordinary kind, because it would require a knowledge of how to alter the composition of the atomic nucleus, and except on an extremely minute scale—as when Rutherford bombarded atoms of aluminium, etc., with α-particles—we have not the faintest idea of how this might be accomplished. If we could do it, all our power problems would be at an end, as already indicated on p. 309. Confronted with the atomic nucleus with its rich possibilities of rearrangement and its vast store of energy, the scientist is, so to speak, in front of an immensely strong locked safe. He has scarcely any tools and has no idea where to find the key. Still he knows now that the safe contains precious things, and he is gazing at it with a curious intentness that was absent a few years ago. One never knows.

Coming back, however, to the question of really likely developments, one asks whether the human race will actually be the happier for all the further great discoveries that the chemist will certainly make. Past experience sometimes suggests a pessimistic note. Chlorine may be used as a wonderful bleaching agent, and ammonia as a source of the fertilizers with which we enrich our fields, but we may make use of both as instruments of war with which to destroy our fellows.

Mr. H. G. Wells sets out the situation very clearly in *The World Set Free,* where man discovers the secret of atomic energy and at first uses the knowledge for warlike purposes, with the result that civilization is well-nigh destroyed. Later he sees his mistake and the discovery becomes of world-wide helpfulness.

There can be no doubt that our progress in the art of living peaceably together is not at present keeping pace with our advance in science, and the great problem is to make it do so. We *shall* solve the problem, though not

perhaps without many failures and set-backs; and success will come all the sooner if we realize that our interest in science should be accompanied with a steady enthusiasm for the ideal of goodwill to men.

APPENDIX

SIMPLE QUALITATIVE ANALYSIS

An important part of the work of the analyst consists in the identification of *salts.* Now a salt is the substance formed when the hydrogen of an acid is replaced by a metal, and as there are hundreds of acids and perhaps fifty or sixty metals, it is evident that the number of different salts must be very large indeed.

However, in what follows we shall deal only with the salts derived from six acids and twelve metals (counting "ammonium" as one). This will greatly simplify the work, but at the same time it will give us some idea of the general principles of analysis.

A salt when dissolved in water gives rise, as we have already seen in Chapter IV, to two ions. Copper sulphate, for instance, gives us copper ion, Cu^{++} and sulphate ion, SO_4^{--}, known respectively as the positive ion or cation (because in electrolysis it appears at the cathode) and the negative ion or anion. They are often referred to simply as the "metal" (or "base"), and the "acid" (or "acid radical"). It does not matter very much which we identify first, but we shall begin with the identification of the acid radical. In the little scheme outlined below, it is understood that this radical is one of the following six:— sulphate, chloride, nitrate, sulphite, carbonate, phosphate. It is understood also that only a simple salt (*i.e.* not a mixture) is being identified.

Practical directions will be given in ordinary type, and notes, explanations, etc. in smaller type.

Identification of Acid Radical

1. If the salt is supplied in solution, boil about half of the latter down to dryness, as the solid is required except where solution is mentioned.

Take care not to heat the dry residue strongly, because a nitrate, if present, would thereby be decomposed. *E.g.*

$$2Pb(NO_3)_2 \rightarrow 2PbO + 4NO_2 + O_2.$$

2. Add hydrochloric acid, and afterwards warm. Violent

effervescence in the cold (carbon dioxide evolved) indicates a *carbonate.* *E.g.*

$$K_2CO_3 + 2HCl \rightarrow 2KCl + H_2O + CO_2.$$

Little action in the cold but effervescence on warming, with evolution of sulphur dioxide, indicates a *sulphite.* *E.g.*

$$Na_2SO_3 + 2HCl \rightarrow 2NaCl + H_2O + SO_2.$$

We recognize sulphur dioxide by its characteristic choking smell. Further, if a piece of filter paper is dipped in potassium dichromate solution and held at the mouth of the test-tube, it is turned green.

3. Add pure conc. sulphuric acid and afterwards warm, but do not boil.

Boiling causes the production of thick acrid fumes, and this would make it impossible to recognize any gases produced by the action of the acid on the salt. Pure acid is used because the "commercial" product often smells of sulphur dioxide.

Carbonate and *sulphite* will give reactions very similar to those described in (i), except that a sulphite would effervesce in the cold.

Effervescence with production of hydrogen chloride indicates a *chloride.* *E.g.*

$$ZnCl_2 + H_2SO_4 \rightarrow ZnSO_4 + 2HCl.$$

Hydrogen chloride is recognized by its characteristic pungent smell, and especially by a steamy appearance outside the test-tube, much increased by breathing across the mouth of the tube.

Faint brown fumes on heating (much more perceptible on looking down into the test-tube, but hold the latter at arm's length) indicate a *nitrate.*

Nitric acid is produced in the first instance, and a little of it is decomposed by the heat. *E.g.*

$$Pb(NO_3)_2 + H_2SO_4 \rightarrow PbSO_4 + 2HNO_3;$$
$$4HNO_3 \rightarrow 2H_2O + 4NO_2 + O_2.$$

4. If the salt was not supplied in solution, dissolve a little in water. If it will not dissolve in water, add a little dilute hydrochloric acid and warm.

Do not decide too hastily that the salt will not dissolve in water. Take only a *little* of the salt with, say, 20 times its bulk of water, and heat. If the salt does not dissolve now, acid may be added.

Add barium nitrate.[1] A white precipitate insoluble in dil. hydrochloric acid indicates a *sulphate*. *E.g.*

$$CuSO_4 + Ba(NO_3)_2 \rightarrow BaSO_4 + Cu(NO_3)_2.$$

(i) Barium chloride is often used instead of the nitrate, but a white precipitate in this case might be due to the presence of a silver salt or a lead salt, giving insoluble silver chloride or lead chloride.

(ii) It is important to make sure that the precipitate is insoluble in hydrochloric acid. Carbonates, sulphites, and phosphates will all give precipitates, but these are soluble.

5. Begin as in the last test, but if acid is necessary, use dilute nitric. Now taking *one or two drops only* of the solution, add a solution of ammonium molybdate in nitric acid, afterwards warming gently. A fine yellow precipitate indicates a *phosphate*.

6. If no definite result has been obtained so far, it is most likely that either a nitrate, a sulphite or a chloride has been overlooked. Try additional tests for these as described in (7), (8) and (9).

7. Mix a little of the dry salt with copper filings, add a few drops of conc. sulphuric acid, and warm. Reddish brown fumes indicate a *nitrate*.

Thus, with lead nitrate, nitric acid is first produced as already described in (3), and this is then reduced by the copper,

$$Cu + 4HNO_3 \rightarrow Cu(NO_3)_2 + 2H_2O + 2NO_2.$$

8. To test for a sulphite, dissolve in water and then boil with a little bromine water. This will oxidize any sulphite present to a sulphate, which will now give the reaction described in (4). The oxidation of sodium sulphite would be represented by the equation

$$Na_2SO_3 + Br_2 + H_2O \rightarrow Na_2SO_4 + 2HBr.$$

[1] *I.e.* a *solution* of barium nitrate, and so throughout this Appendix, when referring to reagents. If solid is intended it will be definitely stated except when there could be no ambiguity (*e.g.* copper). Acids will be distinguished as "conc." or "dil."

9. Dissolve a little of the salt in dilute nitric acid (or add this acid if the salt is already in solution), and then add silver nitrate. A white precipitate, soluble in ammonia, indicates a chloride. *E.g.*

$$ZnCl_2 + 2AgNO_3 \rightarrow Zn(NO_3)_2 + 2AgCl.$$

Identification of Base

N.B.—The bases considered in the following scheme are lead, silver, copper, antimony, arsenic, iron (ferrous and ferric), aluminium, zinc, magnesium, sodium, potassium, and ammonium.

10. Dissolve in water and then add a little dilute hydrochloric acid.

In the case of *antimony,* water will give a milky precipitate of the oxychloride, — $SbCl_3 + H_2O \rightleftarrows SbOCl + 2HCl$. The addition of hydrochloric acid will cause the reaction to proceed from right to left, and a clear solution will be obtained.

A white precipitate indicates *lead* or *silver*. *E.g.*

$$AgNO_3 + HCl \rightarrow HNO_3 + AgCl.$$

Pour a *little* of the precipitate into another test-tube, add water and boil.[1] If it dissolves, *lead* is present (the lead chloride will crystallize out on cooling the test-tube under the tap).

Examine the remainder of the precipitate for silver. If left for a few minutes, silver chloride becomes violet, especially in a strong light.

Add ammonia solution to a little of the precipitate. If it dissolves, *silver* is present (*cf.* (9) above).

Finally, to the original solution add potassium chromate. A dark red precipitate indicates *silver,* a yellow one *lead.*

11. If silver and lead are absent, pass hydrogen sulphide through the solution containing hydrochloric acid.

[1] In more advanced analysis where several bases might be present, the silver and lead would be removed by filtering off their chlorides, and H_2S would be passed through the filtrate. The same principle —successive removal of bases by filtration,—would be employed throughout. Here, of course, we are assuming that only one base is present.

A black precipitate indicates *copper,* an orange one *antimony,* a yellow one *arsenic.* *E. g.*

$$CuSO_4 + H_2S \rightarrow CuS + H_2SO_4.$$

The presence of copper is confirmed by the blue colour of the original solution; antimony by the milky precipitate already mentioned in (10). Arsenic (and also antimony) may be confirmed by Marsh's test, described on pp. 86-7. Before lighting the hydrogen from the generator, make sure that a specimen of it (collected in a test-tube) burns quietly.

12. Boil the solution to expel hydrogen sulphide, and then boil again with a few drops of conc. nitric acid. Add ammonium chloride, and then ammonium hydroxide in excess. A brown precipitate indicates *iron,* a white gelatinous one *aluminium.* *E.g.*

$$Fe_2(SO_4)_3 + 6NH_4OH \rightarrow 2Fe(OH)_3 + 3(NH_4)_2SO_4.$$

(i) If hydrogen sulphide were not expelled, zinc (if present) would be precipitated as sulphide as soon as ammonia was added, because zinc sulphide is insoluble in an alkaline solution.

(ii) Nitric acid is added to oxidize any ferrous salt that may be present to ferric (*cf.* p. 187), because though a ferrous salt is precipitated by ammonia, the precipitation is not very complete. Even if the original salt were ferric, it will have been reduced to ferrous by the hydrogen sulphide. *E.g.*

$$2FeCl_3 + H_2S \rightarrow 2FeCl_2 + 2HCl + S.$$

(iii) Ammonium chloride is added to prevent the precipitation of magnesium at this stage.

(iv) It is easy to tell when ammonia is in excess, because after shaking, the solution will smell of ammonia. When shaking, turn the test-tube away from yourself and other people, for the liquid often spurts out.

13. To find whether the original salt was ferrous or ferric, notice the colour of the original solution. A ferrous salt gives a watery-green solution, a ferric salt, a yellow or brown one.

Also, with a ferric salt, ammonium thiocyanate gives a blood-red coloration, while with a ferrous salt there is no

colour change. A *faint* pink need not be regarded seriously, it only means that a trace of ferric salt has been produced by atmospheric oxidation.

14. To a portion of the alkaline solution obtained in (12) add ammonium sulphide. A white precipitate (coloured yellow with the ammonium sulphide) indicates *zinc*. *E. g.*

$$ZnSO_4 + (NH_4)_2S \rightarrow (NH_4)_2SO_4 + ZnS.$$

15. To another portion of the alkaline solution obtained in (12) add sodium phosphate. A white precipitate indicates *magnesium.*

The precipitate is magnesium ammonium phosphate, $Mg(NH_4)PO_4$.

16. Heat the original substance with a solution of sodium hydroxide. If ammonia is evolved (characteristic smell) the substance was an *ammonium* salt. *E.g.*

$$NH_4Cl + NaOH \rightarrow NaCl + H_2O + NH_3;$$
$$(NH_4)_3PO_4 + 3NaOH \rightarrow Na_3PO_4 + 3H_2O + 3NH_3.$$

17. Dip a platinum wire (or the "lead" extracted from a lead pencil) in a little of the original substance moistened with dilute hydrochloric acid, and hold it in the bunsen flame. A *strong* golden-yellow colour indicates *sodium.*

A violet colour (reddish violet when examined through blue glass) indicates *potassium.*

The blue glass is to absorb yellow light due to traces of sodium compounds present as impurity. The yellow light masks the characteristic potassium colour.

Do not conclude that sodium is present unless (i) the yellow colour is really well-marked, and (ii) you are sure that no other base is present.

To confirm potassium, take a *strong* solution of the salt being tested and add to it a strong solution of tartaric acid. A crystalline precipitate of potassium hydrogen tartrate (cream of tartar) separates out (*cf.* p. 279). Separation is sometimes a little slow, but may often be hastened by scratching the sides of the test-tube with a glass rod. *E.g.*

$$KCl + H_2 . C_4H_4O_6 \rightarrow KH . C_4H_4O_6 + HCl.$$

Table of Solubilities

	Bromide	Carbonate	Chlorate	Chloride	Hydroxide	Iodide	Nitrate	Phosphate	Silicate	Sulphate	Sulphide
Aluminium...	W	..	W	W	A	W	W	A	**A**	W	A
Ammonium...	W	W	W	W	W	W	W	W	..	W	W
Barium......	W	A	W	W	W	W	W	A	A	Ins.	W
Calcium......	W	A	W	W	**W**	W	W	A	A	**W**	W
Copper.......	W	A	W	W	A	W	W	A	A	W	A
Hydrogen....	W	W	W	W	W	W	W	W	W	W	W
Iron (ferrous).	W	A	W	W	A	W	W	A	A	W	A
Iron (ferric)...	W	..	W	W	A	W	W	A	A	W	A
Lead.........	**A**	A	W	A	A	**W**	W	A	A	**A**	A
Magnesium...	W	A	W	W	A	W	W	A	A	W	A
Nickel.......	W	A	W	W	A	W	W	A	A	W	A
Potassium....	W	W	W	W	W	W	W	W	W	W	W
Silver........	Ins.	A	W	Ins.	..	Ins.	W	A	..	**W**	A
Sodium......	W	W	W	W	W	W	W	W	W	W	W
Zinc.........	W	A	W	W	A	W	W	A	A	W	A

NOTES

1. W = Sol. in water; **W** = Sparingly sol. in water.
   A = Sol. in one of the common acids (usually dil. HCl or HNO_3);
   A = Sparingly sol. in acid.
   Ins. = Insoluble in water and acid.
2. It is worth while *remembering* that the following are soluble:—
   (i) All common compounds of sodium, potassium and ammonium.
   (ii) All chlorides, except those of silver, lead and mercury (-ous).
   (iii) All nitrates and chlorates.
   (iv) All sulphates, except those of lead, barium, strontium and calcium (the last very slightly soluble).
3. Carbonates and phosphates, except those of sodium, potassium and ammonium (*cf.* above) are *insoluble*.

Alloys

Composition	Name	Sp. gr.	M.P. (°C)	Chief uses
Aluminium				
90 Al, 10 Mg	Magnalium	2.5	608	Many small light articles (*e.g.* balance beams)
94.4 Al, +Mg+Cu+Mn	Duralumin	2.8	....	Airship construction
Bismuth				
4 Bi, 2 Pb, 1 Sn, 1 Cd	Wood's fusible metal	9.7	65.5	In dentistry
2 Bi, 2 Pb, 1 Sn	Bismuth solder	....	111	Automatic sprinklers; specia soldering
Copper				
90 Cu, 10 Al	Aluminium bronze	7.6	1050	Hulls of yachts, etc. (resists sea-water corrosion)
82 Cu, 15 Mn, 3 Ni	Manganin	8.5	....	Resistance boxes, etc.
90 Cu, 10 Sn	Bronze; gunmetal	8.8	1010	Very varied
80 Cu+Sn+Sb+P	Phosphor bronze	8.8	....	Substitute for steel where corrosion must be avoided.
2Cu, 1 Zn	Brass (ordinary)	8.4	940	Very varied
52 Cu, 26 Zn, 22 Ni	German silver	8.45	....	Resistance coils; imitation silver articles
Iron				
86 Fe, 13 Mn, 1 C	Manganese steel	7.81	1510	Rock-crushing machinery; safes, etc.
96.5 Fe, 3.5 Ni	Nickel steel	....	....	Armour plating of battleships
63.8 Fe, 36 Ni, 0.2 C	Invar	8.0	1497	Clock-pendulums, standard lengths, etc. (coeff. of exp.—almost zero)
94.5 Fe, 5 W, 0.5 C	Tungsten steel	....	....	High-speed drills
Gold				
90 Au, 10 Cu		17.2	940	Coinage
Lead				
82 Pb, 15 Sb, 3 Sn	Type metal	....	....	Printer's type
2 Pb, 1 Sn	Solder	9.4	240	Soldering
Mercury				
70 Hg, 30 Cu	Dentist's amalgam	....	....	Filling teeth
Nickel				
67 Ni, 28 Cu, 4.5 Fe	Monel metal	8.90	1360	Very varied—turbine blades; vessels used in chemical manufacture, etc.
Silver				
90 Ag, 10 Cu		10.3	875	Coinage
Tin				
90 Sn, 10 Sb	Britannia metal	....	260	Plated goods
6 Sn, 1 Sb, 1 Cu	Antifriction	7.53	233	Machine bearings
75 (or more) Sn+Pb	Pewter	....	....	Drinking vessels, etc.

Some Important Temperatures (°C)

Boiling point of water	100	Dull red heat	530
Melting point of ice	0	White heat	1300
Absolute zero	—273·1	Bunsen flame	1870
Body in health	36·9	Oxy-acetylene flame	3000

Physical Constants of some Important Elements

(For atomic weights see inside of back cover.)

Element	*Melting Point °C*	*Boiling Point °C*	*Sp. gr. $H_2O=1$ *Air=1*	*Element*	*Melting Point °C*	*Boiling Point °C*	*Sp. gr. $H_2O=1$ *Air=1*
Aluminium	659	1800	2.71	Magnesium	651	1120	1.74
Antimony	630	1440	6.62	Mercury	−39	357	13.6
Bismuth	269	1436	9.78	Nickel	1452	?	8.90
Carbon (amorphous)	3500	?	1.75 – 2.10	Nitrogen	−210	−195	.967*
Chlorine	−101	−34	2.49*	Oxygen	−218	−183	1.105*
Chromium	1615	2200	6.92	Phosphorus	44	288	1.83
Copper	1083	2310	8.94	Platinum	1755	3910	21.4
Gold	1063	2500	19.3	Silver	960	1955	10.5
Hydrogen	−259	−253	.0695*	Sulphur	113	445	2.07
Iron	1530	2450	7.86	Tin	232	2270	7.29
Lead	327	1525	11.4	Zinc	419	930	7.10

Boiling Points (°C)

Acetic acid	118	Gasoline	70 - 90
Acetone	57	Glycerine	291
Alcohol (ethyl)	78·3	Helium	—268·8
Ammonia	—33·5	Mercury	357
Benzene	80	Sulphur	445
Bromine	59	Sulphur dioxide	—10
Carbon disulphide	46	Turpentine	159
Ether	34·6		

INDEX

N.B.—The principal references are indicated by **heavy type.**

ANSWERS TO NUMERICAL EXAMPLES

Chapter I, pp. 20–23.

9. 511·9 c.c. **10.** (i) 73·3 cm. (ii) 527 c.c.
11. (i) 680 c.c. (ii) 0·0612 gm. (iii) 32·7 gm.
14. 4. **15.** (*a*) 1·17 gm. (*b*) 3·195 gm. (*c*) 0·765 gm.
16. 1·296 gm. *Lighter,* carbon monoxide, methane, ammonia; *heavier,* oxygen, sulphur dioxide, hydrogen sulphide.
17. (*a*) 5·6 *l.* (*b*) 22·4 *l.* (*c*) 11·2 *l.* (*d*) 44·8 *l.*
18. (*a*) 44 gm. (*b*) 14 gm. (*c*) 48 gm.
19. (*a*) 11·2 *l.* (*b*) 14·19 *l.*
20. 4·34 gm.
21. Hydrogen, 66⅔ per cent.; CO_2, 33⅓ per cent.
22. (*a*) 40 c.c. O_2, 20 c.c. CO_2, 40 c.c. steam.
(*b*) As before, but no steam. **23.** 99.

Chapter III, pp. 40–41.

2. 350; 342. **3.** 34·3. **4.** 24·0; 1 atom.
7. 62; 60. **8.** 261 **9.** C_5H_4; 133; $C_{10}H_8$.

Chapter IV, pp. 52–53.

3. −1·86°C.

Chapter V, pp. 63–64.

6. 1559 tons. **7.** 2·35 gm. **8.** 59·5. **9.** 1·77 *l.*

Chapter VII, p. 90.

2. 193·5 tons. **5.** $NaH_2PO_2 . H_2O$.

Chapter VIII, p. 104.

8. 7·66 tons. **9.** $KAlSi_3O_8$.

Chapter IX, pp. 126–127.

4. 93·9 *l.* **7.** 99 tons.

Chapter X, p. 127.

7. 24·4 tons. **8.** $Na_2CO_3 . 10\ H_2O$. **9.** (*a*) 8·91 *l.* (*b*) 17·8 *l.*

Chapter XI, p. 134.

1. 4·03 tons. **2.** 2·37 *l.* **3.** KNO_3, 74·8; C, 13·3; S, 11·9.

Chapter XII, pp. 141–142.

2. (*a*) 38·6 tons. (*b*) 111·4 tons (*c*) 31·8 tons.
3. (*a*) 1,500,000 cu. ft. (*b*) 1,250,000 cu. ft.
4. (*a*) 10·5. (*b*) 18·5.

Chapter XIII, p. 154.

6. 0·157 tons (=3·14 cwt.). **7.** 40·9 *l.*
8. 2 million cu. ft.

Chapter XIV, pp. 165–166.

6. 269·4 tons. **7.** 7. **10.** (*a*) HgCl. (*b*) Hg_2Cl_2.

Chapter XV, p. 176.

1. 276 tons. **7.** 183·7 gm. **8.** $K_2SO_4 . Cr_2(SO_4)_3 . 24H_2O$.

Chapter XVI, pp. 195–196.

7. 70 and 72·4 **8.** 27·8 oz. **9.** $2Fe_2O_3 . 3H_2O$.
10. 3·38 tons. **11.** 1622 *l.*

Chapter XVII, p. 209.

3. Ag_3SbS_3. **6.** 1028 c.c.

Chapter XVIII, p. 222.

8. 47,000 tons, (nearly). **9.** $(PbCO_3)_2 . Pb(OH)_2$.
10. 1·03 *l.* **11.** Pb, 47·8; As, 26·0.

Chapter XIX, p. 229.

4. 3·30 kg. **5.** 196·9.

Chapter XX, p. 236.

1. 8·12 tons. **7.** 1·58 gm.

Chapter XXI, p. 245.

2. 10 cu. ft. **3.** (i) C_2H_5. (ii) C_4H_{10}.
7. 5·57; 525. **8.** Methane.

Chapter XXII, p. 254.

3. 11,240 tons.

Chapter XXIII, pp. 264–265.

1. (i) C, 44·4; H, 6·2; O, 49·4.
(ii) C, 42·1; H, 6·4; O, 51·5.
2. (i) CH_2O. (ii) $C_6H_{12}O_6$.

Chapter XXIV, p. 273.

2. 50·5 gm. **4.** $C_{10}H_{16}$.

Chapter XXV, pp. 283–284.

1. (i) C_2H_4O. (ii) $C_4H_8O_2$. **2.** 4·48 oz. **3.** 5·57 *l.*

Chapter XXVI, p. 293.

5. 10·4 gm.; 17·0.

Chapter XXVII, pp. 297–298.

1. 226·1. **2.** 225·9.

dil
$2HNO_3 \rightarrow H_2O + 2NO_2 + 3[O]$ } N.B

HNO_3

The Commoner Elements and their Atomic Weights

Element	Symbol	Atomic Weight (approximate)	Atomic Weight (more exact)
Aluminium . . .	Al	27	26·97
Antimony (stibium) .	Sb	122	121·77
Argon . . .	A	40	39·91
Arsenic . . .	As	75	74·96
Barium . . .	Ba	137	137·37
Bismuth . . .	Bi	209	209·00
Boron . . .	B	11	10·82
Bromine . . .	Br	80	79·92
Cadmium . . .	Cd	112	112·41
Calcium . . .	Ca	40	40·07
Carbon . . .	C	12	12·00
Chlorine . . .	Cl	35·5	35·46
Chromium . .	Cr	52	52·01
Cobalt . . .	Co	59	58·94
Copper (cuprum) .	Cu	64	63·57
Fluorine . . .	F	19	19·00
Gold (aurum) . .	Au	197	197·2
Helium . . .	He	4	4·00
Hydrogen . . .	H	1	1·008
Iodine . . .	I	127	126·93
Iridium . . .	Ir	193	193·1
Iron (ferrum) . .	Fe	56	55·84
Lead (plumbum) .	Pb	207	207·2
Lithium . . .	Li	7	6·94
Magnesium . .	Mg	24	24·32
Manganese . .	Mn	55	54·93
Mercury (hydrargyrum)	Hg	201	200·61
Neon . . .	Ne	20	20·2
Nickel . . .	Ni	59	58·69
Nitrogen . . .	N	14	14·01
Oxygen . . .	O	16	16·00
Phosphorus . .	P	31	31·03
Platinum . . .	Pt	195	195·23
Potassium (kalium) .	K	39	39·10
Radium . . .	Ra	226	225·95
Selenium . . .	Se	79	79·2
Silicon . . .	Si	28	28·06
Silver (argentum) .	Ag	108	107·88
Sodium (natrium) .	Na	23	23·00
Strontium . .	Sr	88	87·63
Sulphur . . .	S	32	32·06
Thorium . . .	Th	232	232·15
Tin (stannum) . .	Sn	119	118·70
Tungsten (wolframium)	W	184	184·0
Uranium . . .	U	238	238·17
Zinc . . .	Zn	65	65·38

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